STUDY ON OPTIMUM CONDITIONS FOR DIESEL SPILL REMOVAL APPLICATION BY A NATURAL RESOURCE-PEAT

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Study on Optimum Conditions for Diesel Spill Removal Application by a Natural Resource – Peat

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Abstract

The balance between energy demand and the conservation of natural resources is a worldwide issue that people have been confronted with for over a thousand years and will continue to be an issue for future generations. Consequently the environment has been more or less destroyed by human activities with the boom of industrialization and modernization especially for non-renewable natural resources. Environmental problems such as increasing global population, water resource shortage, greenhouse gas emission and oil spills have persisted due to the unlimited human demands on obviously limited natural resources.

Contamination due to discharges from various manufacturing outfits and environmental degradation due to exploration and other associated highly economic human activities have resulted in consistent pollution problems requiring urgent attention. Many oil clean-up treatments have been developed and proved to be effective both in the laboratory and real situations, but the factorial analysis of diesel removal application under different weather and water environments might be a new research field. This study is based on the idea of using peat as an environmentally friendly material with easy application to clean up diesel-contaminated water from freshwater bodies especially lakes and rivers with low water turbulence.

An experimental water environment was simulated using varied impact factors such as water temperature, water turbulence and added diesel volume. A 200mL beaker was placed in a 2L cuboid tank which was filled with ice cubes to realize the simulation (for those combinations with 4 °C). A 75mL sample of lake water and diesel was added

to the beaker to simulate the water body, the 2L cuboid tank was filled with ice cubes and a thermometer was inserted to adjust the environmental temperature under selected combinations. Two types of peat (poorly humified and highly humified) were applied on simulated contaminated water with different combinations of factors that could have an effect on the remaining Total Petroleum Hydrocarbons (TPHs) in the water. TPH analysis was conducted in the laboratory of Maxxam Analytic Inc., St. John's. Optimum external conditions and both floating and dissolved oil removal efficiency were analyzed and obtained.

Peat showed a high adsorbing ability as it could adsorb diesel at least 2.6 times its weight in water, and the diesel removal efficiency could be as high as 99.99% with optimum treatment conditions. Experimental results and statistical analysis using Design Expert 7.0® and Minitab 15® showed the optimum condition for high removal efficiency was to apply fine horticultural peat for 0.25 h which could remove 99.99% of floating diesel and 82.03% of dissolved diesel. The average remaining TPHs in the treated contaminated water under different external conditions was 3.3mg/L, which was considerably lower than the Newfoundland Disposal Limit indicated as 15mg/L. Short-time application, lower water turbulence and lower water temperature were suggested to obtain lower remaining TPHs.

This study analyzed the optimal conditions for applying peat on the surface of diesel-contaminated water. Experimental results and analyses showed that lower water turbulence and lower water temperature were appropriate conditions for the removal of

diesel by using peat and shorter reaction time between the peat and diesel was preferred to obtain less remaining TPH in the water.

The reaction mechanisms between functional groups on peat particle surface and oil droplets were not investigated. Other meteorological factors such as wind and marine water were not included in the current experiment.

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List of Abbreviations and Acronyms

Ads.	Adsorbed oil concentration
ANOVA	Analysis of Variance
API	American Petroleum Institute
BOD	Biological Oxygen Demand
CCME	Canadian Council of Ministers of the Environment
CIS	the Commonwealth of the Independent States
COD	Chemical Oxygen Demand
ERC	European Research Council
FAO	Food and Agriculture Organization of United Nations
FID	Flame ionization detector
g	Gram
GC	Gas chromatograph
H	Horticultural peat
h	Hour
HD	Highly decomposed peat
HMRAD	Hazard Material Response and Assessment Division
INCA	Indian and Northern Affairs Canada
Ini.	Initially dissolved oil concentration
L	Liter
mL	Milliliter
MS	Mean square
MSW	Within groups mean square
MSDS	Materials Safety Data Sheet
NMED	New Mexico Environment Department
NOAA	National Oceanic and Atmospheric Administration
NPS	National Park Services
OCED	Organization for Economic Co-operation and Development
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
RBCA	Risk Based Corrective Action
rpm	revolutions per minute
SS	Sum of squares
Temp.	Water temperature
TPHs	Total Petroleum Hydrocarbons
TSSs	Total Suspend Solids
Vol.	Volume

1 Introduction

For over half a century now, oil has dominated the energy market, replacing coal. The consequences of this include rapid and dramatic technological changes to peoples ideas and perceptions about the environment. Green technology, health and the environment have gradually emerged as the leading trends in global development. Saving natural resources, protecting the environment and building a more harmonized global village for the present and future generations is becoming not only a social responsibility but a legitimate target. Consequently, conventional and traditional treatment methods for solving environmental problems are facing challenges. Natural and recyclable/reusable materials are beginning to attract greater attention as possible supports in managing contaminants/pollutants.

The fragility of the environment and ecosystem has been compounded and made even more complex by unpredictable oil spill accidents caused by increasing consumption of oil. Peat – a reproducible and natural resource – might be a good replacement for chemical dispersants and other power machines such as skimmers, to clean up oil spills. Although its application has been known to be limited by weather conditions and type of oil, the high cost-effectiveness and high adsorbing ability of peat make it a preferable and attractive sorbent when compared to other traditional physical and chemical methods.

1.1 Peat – an Introduction

As a combustible natural resource, peat has been burnt directly or transformed into a liquid fuel as an alternative energy for years (Smith et al., 1975; Clemens et al., 1982). Recent research showed that diesel-contaminated peat could also be burnt, with the high heating value of the contaminated material being comparable to that of coal (Ghaly et al., 1999). However, in addition to being an energy source, peat also performs well in the environmental field, where treated or untreated forms of it are used as a sorbent with high absorbing ability and removal efficiency for most contaminants such as heavy metal contaminated water, municipal sewerage and oily contaminated water (Dissanayake and Weerasooriya, 1982; Bord Na Mona, 2001; Suni et al., 2004; Pérez et al., 2005).

1.2 World Oil Spill Accidents – a Brief Review

Although William Marsden (2009) argued in his latest report that the age of oil is approaching the end, oil still remains the natural energy resource most relied upon by human beings. **Table 1-1** shows the decreasing trend of numbers of oil spill accidents in recent decades (mainly caused by tanker accidents, oil spill caused by war in the Persian Gulf, 1991 was not included), which is not a function of the end of the oil era, but as a result of improved and developed technology. The other factors include increasing environmental concerns and efficient regulatory policies. Though environmental concerns have been spreading, millions of tons of oil have still accidentally found their way into our environment (ITOPF, 2009).

Table 1-1 Historical data of oil spill accidents (ITOPF, 2009)

Year	Number of oil spills		Rate of decline (%)		Quantity of oil spilled	Rate of decline
	7-700 Tons	>700 Tons	7-700 Tons	>700 Tons	(Tons)	(%)
1970s	540	253			3,140,000	
1980s	359	93	33.5	63.2	1,177,000	62.5
1990s	282	79	21.5	15.1	1,136,000	3.5
2000s	140	33	50.3	58.2	206,000	81.9

1.3 Problems

At sea or in inland freshwater environments, where most oil spill accidents have occurred, they could cause, and definitely have caused a series of catastrophes to the environment affecting plants, animals and human beings. Some notorious events in the environmental field, such as millions of barrels of crude oil spilt in the Persian Gulf in 1991 (Khordagui and Al-Ajmi, 1993), the recent BP Gulf of Mexico oil spill and the Exxon Valdez event have been estimated to last for decades (NOAA/HMRAD, 1992; BP, 2010). To some degree, long-term, invisible oil seepages could be worse to the environment than those visible oil spill accidents that are frequently reported, since the situation might already be out of control by the time they are discovered. For instance, a long-term, slow oil spill leakage that occurred in Africa was reported to have affected the ambient environment for nearly nineteen (19) years (Obot et al., 1992).

The application of peat as a filter or natural sponge for cleaning up landfill leachate, domestic wastewater and oily contaminated water has been studied for several years and the results suggest that peat is efficient in removing contaminants from water (Cohen et al., 1991; Corley et al., 2006; Rizzuti et al., 1996; Suni et al., 2006; Viraraghaven and Mathavan, 1988 and 1990). However, in some cases, peat could not

perform its maximum adsorbing capability due to weather and water conditions. Therefore, large quantities of chemical agents have been applied to the oil spills in order to obtain a high level of removal efficiency without taking into consideration of the long-term environmental impact. With the introduction of chemical agents into the water environment, the risk of harm to aquatic animals and plants has been increasing (Bhattacharyya et al., 2002). The aim of the present study is to test the contaminant removal efficiency of peat under varied water and weather conditions, in order to harmonize the long-term environmental benefit and short-term, badly-needed removal efficiency. In addition to investigating the removal process of floating oil film, the study also tested removal efficiency for dissolved diesel by using peat. Another important aspect of the study is to investigate the potential effects of meteorological or water environment on the removal application, and possible solutions for these effects in order to obtain maximum or optimum diesel removal effectiveness by using peat.

1.4 Organization of the Thesis

Chapter 1 briefly introduces oil spill problems which derived from the increasing demand for energy and the potential of peat as an effective material employed in various contaminant removal situations.

Chapter 2 is the literature review that discusses oil spills and oil-water mechanisms after these accidents. This chapter also specifically describes various applications of peat in the environmental field, especially for oil spill removal applications. Government guidelines in some regions and selected previous research are

used as a reference to indicate the efficiency of current experiment. At the end of chapter 2, there is a short introduction to Design Expert 7.0®, Minitab 15® and the Gas Chromatograph - Flame Ionization Detector (GC-FID) used in the designing and interpretation of data from the experiments carried out in the study.

Chapter 3 covers the aims and methods of the current experiment. Detailed experimental procedures for all tests are presented.

Chapter 4 shows the comparison between experimental results and selected governmental guidelines which indicates the high adsorbing ability and removal efficiency of peat. This chapter also presents the results and analyses from batch tests and the detailed interpretation for a two-level factorial experimental design. Regression analyses were conducted for the initially dissolved oil tests and showed the adsorbing versatility of peat under various experimental conditions.

Chapter 5 summarizes the results based on each factor and gives suggestions for future work.

2 Literature Review

2.1 Current Situation of World Energy

Oil has replaced other energy sources and become the most important natural resource for humans since the 1960s. Over the same time petroleum products have been the most important chemical raw materials and industrial consumables for every country regardless of political or economic reasons in the time of integration of global industrialization, and they have never been replaced (EIA, 2009).

In terms of cost, performance, accessibility and popularity, petroleum products will remain the main energy resource for the foreseeable future. This implies that oil spill accidents will continue to occur, and clean-up action must be undertaken within a reasonable time frame.

Figure 2-1 shows the increasing main worldwide energy demands over time, and no doubt the development of technology to provide a better life quality for human beings has contributed to this increase. According to the chart, besides the conventional energy, geothermal, solar, wind and wood (shown as other in Figure 2-1) defined as new energy has been increasingly applied. For 40 years, oil has remained the dominant energy resource. It has been reported that if energy demands in the main world regions had remained at their 1990 level, in 2006 the world would have consumed the energy

equivalent to 4.4×10^9 Tons of Oil. This number will increase with the global population explosion (WEC, 2008).

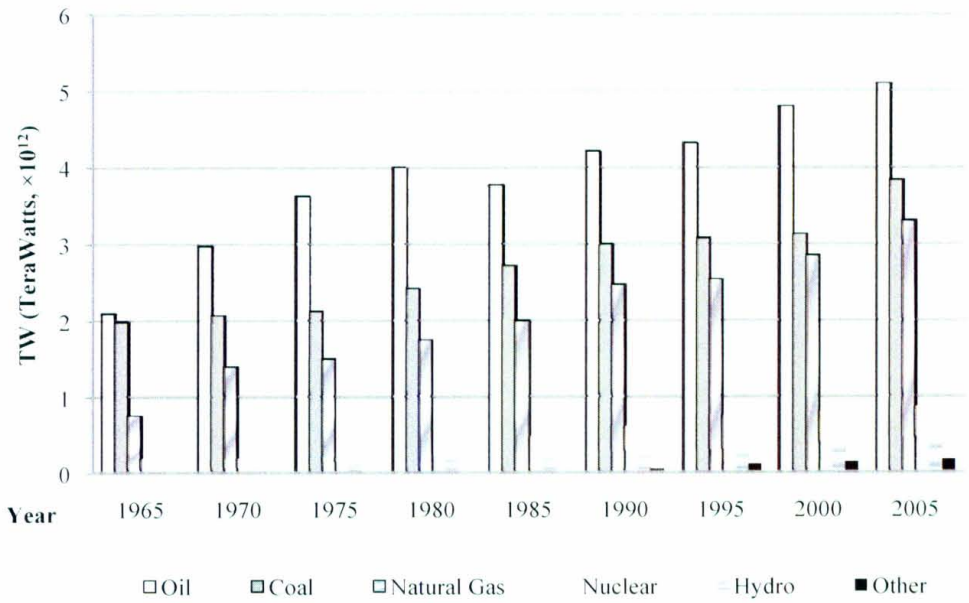


Figure 2-1 World energy demand (adapted from BP, 2006 and EIA, 2009)
Note: the energy type of "other" in the chart include geothermal, solar, wind, and wood; the order of the energy source present in the chart is the same order as the legend

The percentages of fossil energy use compared to all other sources of energy in various regions such as the Organization for Economic Co-operation and Development (OCED) and Commonwealth of Independent States (CIS) are shown in **Table 2-1**. Though new types of energy have been increasingly developed and applied, the fossil energy, which is considered as a conventional type of energy source, still holds a large percentage of the market in several regions. This means there is still a great possibility

for the fossil energy to be a potential contaminant source in the world. The table summarizes the percentage of fossil energy (natural gas, crude oil, petroleum products and coal) of all types of energy sources, and the percentage of petroleum products and crude oil of all fossil energy sources. The percentages of petroleum products and crude oil compared with the other fossil energy sources show that oil has remained the main energy source in most of the regions (World Energy Assessment, 2004). Due to increasing demand oil requires effective and environmentally friendly applications to prevent, protect against, and clean up potential oil spill accidents.

Table 2-1 Primary energy use in various regions (adapted from WEA, 2004)

Energy Types	Regions and percentages (%)					
	OECD[3]	CIS[4] and Eastern Europe	Sub-Saharan Africa	Latin America and the Caribbean	Asia Pacific	Middle East and North Africa
Gas	21.3	42.9	2.5	15.8	7.3	26.7
Crude oil	40.4	24.4	11.8	48	24.5	51
Petroleum products	0.5	5.7	1.1	8.1	1	19.8
Coal	20.8	17.7	20.9	3.8	39	1.7
Fossil energy[1]	83	90.7	36.3	75.7	71.8	99.2
Crude oil and petroleum[2]	49.3	33.2	35.5	74.1	35.5	71.3

[1]: the percentages of fossil energy of all sources of energy in the region
[2]: the percentage of crude oil and petroleum products of the resource of fossil energy
[3]: Organization for Economic Co-operation and Development
[4]: the Commonwealth of the Independent States

2.2 Oil Spill Mechanisms

To investigate oil removal applications, the routes by which hydrocarbon fractions enter the water environment after oil spill accidents must be known to help improve the decontamination process. Oil spill mechanisms are to a great extent determined by the weather and by water conditions. The characteristic of the oil is another dominant factor. After the oil has spread out and formed an oil slick, further changes take place due to a combination of meteorological and hydrological impacts, mainly related to the power of the dominant wind, waves and current. Storms and active turbulence could speed up the dispersion of the oil slick. In narrow coastal zones or shallow waters, some of the oil could be adsorbed on the suspended materials and deposited down to the sediment, since particulates are abundant in such areas (Patin, 1999).

Generally, the primary ways in which these contaminants enter the environment are shown in **Figure 2-2**. Emulsification occurs beneath the surface of the water under the synergetic effects of sorption and dispersion; this happens when oil droplets interact with particles suspended in the water. In a study cited by Enger and Smith (2008), it was reported that approximately 50% of the oil spread out and was biodegraded on beaches or in the water, 20% was evaporated into the air, 14% was recovered by various clean-up treatments, 12% was at the bottom of the sea, 3% lay on the shoreline and 1% still drifted in the water column.

Dissolved oil is highly risky and toxic for aquatic plants and animals when inhaled or digested. Polycyclic Aromatic Hydrocarbons (PAHs) contained in diesel or derived from other petroleum products are carcinogenic (cancer producing), tumorigenic

(able to produce tumors) and teratogenetic (cause birth defects due to interference with growth mechanisms), therefore removing dissolved oil or reducing the concentrations in order to meet limitations or guidelines is important for protecting plankton, larvae and eggs from potential risks. In addition, floating oil slicks are considered to be a potential source of

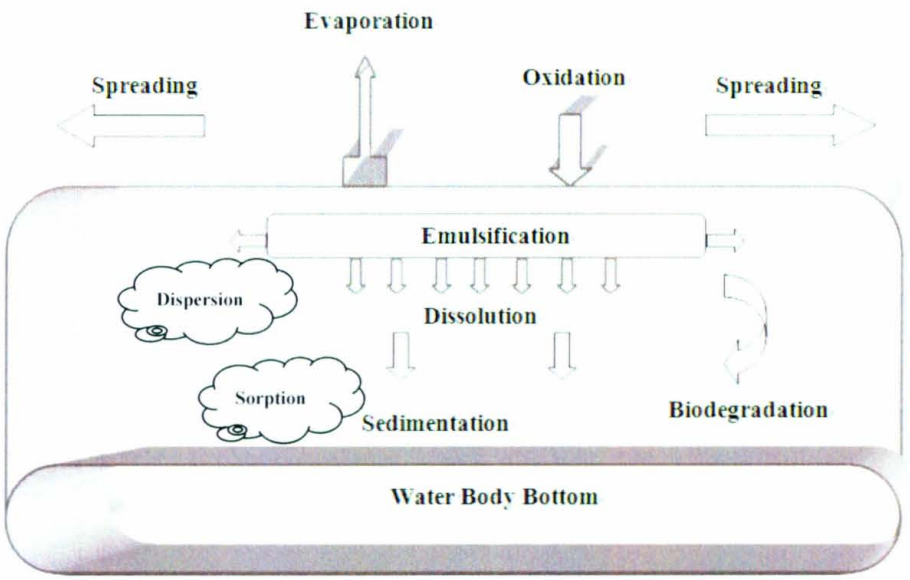


Figure 2-2 Schematic transportation process of spilled oil (adapted from ITOPF, 2002)

air pollution after an oil spill accident. Strong winds or currents and high temperature would enhance the evaporation of hydrocarbons into the air. Water temperature in tropical areas is higher on average than that in frigid zones which could easily cause evaporation. Birds flying into or within the polluted zone are endangered due to the inhalation of highly concentrated PAHs in the air. High concentration of PAHs were found after major oil spills in most of subtidal regions which could be highly dangerous to human and other creatures (Lee and Page, 1997). It has been reported that

Polychlorinated biphenyl (PCBs) and PAHs were both found in sea birds (Walker et al., 1993 and EPA, 1999).

2.3 Marine and Freshwater Oil Spills

2.3.1 Marine Oil Spills

Apart from a fall in the early 1980s during the worldwide economic recession, seaborne oil trade has grown steadily from 1970 to 2010 (ITOPF, 2010). Over 1.5 billion tons of crude oil and oil products are transported each year by more than 7,000 tankers and as a result the estimated input of oil into the marine environment is 3.2 million tons every year (Ghaly and Pyke, 2001). Recent data from ITOPF shows approximately 3.3 spills (over 700 tones) per year on average from 2000 to 2009 (ITOPF, 2010).

Oil leakage could be caused by ship damages, the failure in pipelines operations, production accidents and the loading of oil or the potential risk of underground oil tank corrosion in gas stations (Kowalski et al., 2002). Most of the past serious oil spill accidents occurred in inshore areas and were caused by super oil tanker collisions or human error (Shaheen, 1984). Because the accidents took place near the coast with a huge amount of crude oil being spilled, serious damage to the environment as well as marine animals has always been reported. The costs of follow-up cleaning processes are

dramatically high and hundreds of people could be involved in the complicated and arduous tasks (Shaheen, 1984).

An oil spill in marine water is believed to be one of the worst accidents in the oil industry and environmental field. Oil spill accidents are worse under bad weather and water conditions requiring tons of sorbents, booms or dispersants for clean up. Chemicals such as dispersants are also helpful and highly effective for removing oil from water but invisible long-term bio-accumulation effects remain an issue (Kingston, 2002). Research was carried out on the effect of oil spills from vessels in waters around the United States on the marine ecosystems in marine protected areas; these areas were found to be at risk (Dalton and Jin, 2010).

Marine ecosystems are made up of complex interrelations among aquatic plants, animal species and the physical environment. Spilt oil and petroleum fractions therefore directly affect the food chain creating ecosystem in-balance resulting from bio-magnification (EPA[h], 2008, Gin et al., 2001).

Some of the marine organisms have the ability to swim away from a spill by going deeper into the water or further out to sea while others such as dolphins, turtles, seals and shrimps, living closer to the shore or coast are exposed to toxic substances leading to their death. Oil might sink down to the sediment, where it impacts the habitat

for coral reefs and some sea grasses which are foods for some organisms that could be directly contacted by humans as food or through recreation (EPA[b], 2008).

2.3.2 Freshwater Oil Spills

On the other hand, freshwater oil spills cannot and should not be ignored, although public attention to such types of contamination has been less than to marine water oil spill pollution because they are not easily noticed. Some of the reasons why freshwater contamination is less noticeable to the public could be: the extent of contamination in terms of spread, the volume of the contaminants involved and usually less costly clean-up efforts compared to marine oil spills (API, 1994; Bradley, n. d; EPA[a], 2008).

Freshwater oil spills could impact more negatively on the environment due to the more complicated presence of human-related food chains and trophic levels in freshwater environments (EPA[a], 2008).

The bottom of a still water body serves as the home and breeding ground to many organisms, worms and insects. It is also the food source for organisms and higher animals. Oil in sediments might be extremely harmful because the accumulation of hydrocarbon contaminants could cause a high concentration of toxic substances such as Polycyclic Aromatic Hydrocarbons (PAHs). Once the organisms are contaminated by

these toxic substances, bio-accumulation of these harmful contaminants would magnify their toxic effects to other higher level species in the food chain. This type of contamination and accumulation occurs in standing water bodies with little or no water movement such as lakes, marshes and swamps, which are believed to be the habitats most sensitive to oil spills (EPA[a], 2008).

In the open water, frogs, fish, reptiles and water-fowl would be directly affected by an oil spill once such an accident occurred. In addition, the oiling of plants and grasses that were rooted or floating in the water could occur, harming both the plants and the animals that depend on them for food and shelter. Fisheries located in freshwater are also subject to the toxic effects of oil (EPA[a], 2008, Bhattacharyya, et al., 2002).

Table 2-2 is a summary of serious oil spill accidents that happened in marine water and freshwater, and the clean-up applications. Burning is one of the methods commonly used to remove heavy oil slicks from the surface of open water, especially the sea. However, consideration of human health must be addressed by analyzing the results of the contaminated air plume model before applying this method since PM^{10} (fine particulates < 10 μg) could be transported downwind (NIST, 1994). A high concentration of PM^{10} in the air could have significant health impacts including coughs, asthma, bronchitis and other respiratory illnesses, and mortality (MFE, 2003). It is recommended when the situation was extremely dangerous and clean-up crews were not

able to get close to the accident site. The environment would take a long time to recover after *in-situ* burning. Dispersants proved to be effective but the introduction of chemical agents was of great concerned. Booms were physically easy to apply; they were effective when applied with other physical or chemical removal processes. Improper or late application might cause long-term environmental problems with the wasting of time, cost and labor. The advantages and disadvantages of physical and chemical methods are described in detail in **Section General Decontamination Processes**. Some advanced technologies were employed in the oil spill control and removal process such as advanced model monitoring, simulation and forecasting. Montero et al. (2003) reported the importance of emergency response after an oil spill incidence. All reactions composed an oil removal process. This thesis focuses on oil removal efficiency and external conditions.

Due to these oil spill accidents, people have been looking for a perfect material or method to remove oil effectively and completely. From the angle of philosophy, there is no perfect thing, but to some degree, peat with its high contaminant-adsorbing capability, is an ideal material for marine and freshwater oil removal applications because it is a natural material that can be easily accessed, processed with simple technology, shipped to the contaminated site and then removed after the application. Its characteristics as a cheap and environmentally friendly material have gradually been attracting public

attention. However, peat has to be stored in a dry place and a large volume has to be employed for a big oil spill, which was recommended by a commercial sorbent peat seller (Elcosorb, 2001). Applying peat on the surface of the water could also be highly affected by weather such as strong winds or water turbulence (Spill Sorb, 1998).

2.4 General Oil Decontamination Processes

2.4.1 Physical Treatments

Physical removal methods are usually the first step when an oil spill occurs, regardless of the place, because of their relatively low risk and ease of application (Shaheen, 1984). Several treatments have been applied for trapping and containing oil slicks including booms and sorbents. Booms are floating materials that have shown great efficiency in containing hydrocarbon contaminants when properly applied. The efficiency of booms depends on the time elapsed since the oil spill they are applied. Wind direction must also be considered when applying booms to contain oil slicks, which suggests that booms should be deployed down-wind from an oil spill at the quickest time possible (Shaheen, 1984).

Synthetic sorbents have been widely used in most enclosed environments of oil spills with adsorbing ability between 8 and 30 times their own weights. Some synthetic materials such as polypropylene and polystyrene have been reported to be more efficient

than natural materials such as straw because they performed well in hydrophobic and oleophobic environments. Some of these synthetic substances could be recycled and reused after a series of treatments. However, air contamination during manufacture and how to properly dispose of tons of contaminated sorbents are some of the problems that cannot be ignored (Shaheen, 1984; Mihelcic et al., 2003).

Skimmers have been employed in minor spillages, especially in controlling oil leaks in harbors. Floating pumps have been used to suck the oil slick away from the site. Oleophilic belts have been used to capture the oil by adhesion, the waste (mixed oil and water) eventually being pumped into a tanker or on-site storage (Shaheen, 1984).

2.4.2 Chemical Treatments

Chemical methods are usually employed to improve/enhance the removal application of the physical methods or clean up of special accidents based on the properties and composition of the spilled oil.

Table 2-2 Comparison of cleanup procedures among accidents

Accidents			Cleanup Procedures			
	Year and Name	Spilled Amount (total barrels)	Burning	Dispersants	Booms	Other Removal Approaches
Marine water oil spill	1969, Santa Barbara[1][2][6]	11,200 metric tons crude oil (100,000)	No	Failed	No	Spilled well was plugged by cement and covered by hoods and tents; straw was applied to suck oil slick and collected after.
	1978, Amaco Cadiz[1][2][6]	70 million gallons crude oil (1,619,048)	No	No	Failed	It was reported that all efforts failed since cleanup application was far behind the technology used in the ship.
	1991, The Arabian Gulf Oil Spill[1][2][6]	7,000 – 10,000 barrels crude oil per day for months (9,000,000)	No	Failed	Yes	Precious time for effective cleanup application was terribly lost. Fishing was banned and desalination plants were closed.
	1983, Spanish Super Tanker Castillo de Bellver[1][6]	140,000 tons of crude oil (1,022,000)	No	No	No	It was reported that few cleanup applications were conducted because of dangerous situation.
	1989, Exxon Valdez[2][6]	240,500 barrels of crude oil (240,500)	Yes	Failed	Yes	Oil slick was collected by skimmers and pumped into storage tankers. Bioremediation and sorbents were applied as well.
	2002, Prestige-Nassau[3][6]	10,000 tons of crude oil (73,000)	n.a.	n.a.	n.a.	Simulation models were applied to forecast the movement of oil slick.
Freshwater oil spill	1988, Shell Oil Complex[2]	8,700 barrels of crude oil (8,700)	No	No	No	Oiled vegetations were cut by manual labors and machines. Wildlife was taken to treatment centers for further medical treatment.
	1970, Nigerian long-term oil seepage[5]	n.a.	Yes	No	No	Long-term environmentally adverse effects on plant production were reported 19 years after the oil spill; no cleanup procedures were reported.
	2002, PeeJay Field Oil Leakage[4]	200 m^3 of crude oil (1,256)	n.a.	n.a.	n.a.	This case focused on the improvement of the emergency response system through this accident.

Notes: [1]: Shaheen, 1984; [2]: EPA, 1989 and NOAA/HMRAD, 1992; [3]: Montero et al., 2003; [4]: BCOGC, 2002; [5]: Obot et al., 1992; [6]: USGS, 2005

Treatments include gelling, oil sinking and treated clays, etc. Gel is used for solidifying certain liquids. Oil spills could be minimized by gelling and making the mixed substances not to flow any longer due to this special application (Shaheen, 1984). In some cases, oil is made to sink down to the bottom of the water body by adding sinking powders or granular substances, which bond strongly with oleophilic and hydrophobic materials.

It has been reported that the mixture of diesel and cleaner or dispersant could have a pronounced adverse impact on freshwater marsh microcosms. Although this conclusion was drawn under the "worst" experimental conditions (with no wind, water exchange or wave actions), it still brings with it a warning against applying particular dispersants or chemical treatments which could be highly detrimental for the environment (Bhattacharyya, et al., 2002).

The use of chemical treatments such as dispersants and chemical sorbents has been critically defined and mandatory tests must be conducted before the application of new products. The Sea test and the Rocky Shore test are two toxicity tests which compose the United Kingdom statutory approval scheme for oil spill treatment products (Kirby and Law, 2008).

Chemical methods have been reported to be very controversial as some countries and organizations strongly support their use while others are completely against them. The chemical approach has been suggested for use at open sea rather than in shallow bodies of water (Shaheen, 1984; NOAA/HMARD, 1992).

2.4.3 Other Treatments

Rather than conventional chemical and physical oil removal methods, new advanced technologies have been applied to clean up oil spills such as using new materials or biological treatments.

More and more environmentally friendly products that have the characteristics of being natural and recyclable, and even some industrial or domestic wastes, have been tested in the laboratory or applied in oil spill accidents and could be used instead of chemical treatment such as dispersants. Treated sawdust has been tested and approved to be an effective sorbent compared with conventional sorbents (Banerjee, et al., 2006).

Biological treatments have been analyzed in the laboratory to test the removal ability for various types of oil. When using fungal biomass the pH proved to be the dominant factor that could have a significant effect on oil removal efficiency. The lower the pH was, the better the oil removal efficiency that could be obtained. Adsorbent dosage, water temperature and oil concentration have different removal effects on various types of oil (Srinivasan and Viraraghavan, 2010).

Although physical and chemical treatments have been applied for several years as major treatments, even new technologies have been increasingly introduced in oil removal treatments, environmental concerns have forced people to look for new natural and low-energy materials as suitable replacements. It has been reported that applying peat as a sorbent is superior to others methods because of its low cost and ease of handling during and after application (Cohen et al., 1991; Corley et al., 2006; Rizzuti et al., 1996; Suni et al., 2006; Viraraghaven and Mathavan, 1988; Viraraghaven and

Mathavan, 1990). The availability of peat in Newfoundland makes it an attractive raw material for further investigation as an oil contaminant remover.

2.5 Peat

Peat is highly organic, providing a substantial absorptive and ion exchange capacity; it is a medium for microorganisms, a fibrous material for filtration, and has high water retention capacity (Frostman, 1995). Lee et al. (2001) indicated that peat contains a vast myriad of chemical species and groups including carboxylic acids, phenolic groups, ketones and alcohols. Based on specific chemical and physical reactions among contaminants and peat functional groups, reactions such as chelation, complexation and adsorption enable peat to act as an adsorbent or filter for removing heavy metals, hydrocarbons, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Suspended Solid (TSS) from contaminated water (Cohen et al., 1991). Generally speaking, fibric sphagnum peat is rich in carboxyls, while humic and fulvic acids predominate in sapric peat (Léon-Etienne, 2003).

The various uses of peat are determined by its type and level of decomposition. Weakly decomposed peat composed mainly of Sphagnum mosses is the preferred product for horticultural operations (CSPMA, 2008), while highly decomposed peat is preferred as a combustible fuel (ERC, 1995). Canada signed up to the Kyoto Treaty in 2002 and needs to reduce carbon emissions to 6% below 1990 levels by 2010, which required more environmentally and efficiently natural resource, peat might be a good alternative energy from this aspect (OCR, 2005).

Canada is one of the main peat export countries and has large peat deposits due to its unique natural resources and the combination of the climatic and topographic conditions. The United States continues to represent 85 to 90 percent of the export market for Sphagnum peat produced in Canada (CSPMA, 2008). A report by the Energy Resource Commission indicated that Canada is the third largest producer of horticultural peat in the world and the value of peat production in 1992 was approximately U.S. $110 million (ERC, 1995).

The application of peat in power stations as a power resource has been developed in countries which have considerable peat resources and appropriate energy requirements such as Finland and Ireland. Peat fuel is an economical and more environmentally friendly substitute for coal (PRL, 2008).

Peat could be widely applied in the life of the human being as described above. However, it is necessary to protect this specific natural resource in order for it to be sustained.

2.5.1 Peat Classification

Table 2-3 is a typical peat classification based on the physical appearance of peat in terms of decomposition.

Table 2-3 Peat classification according to degree of decomposition (Dengiz et al., 2009)

Degree of Decomposition	Structure of peat	Presence of humus	Amount of water
Fibric (poorly humified)	Spongy or fibrous, occasionally compacted, felty.	None or very little humus, as dispersed dark mass saturating and coloring plant remains.	Large amount of water, easily trickles out, usually almost clear or only slightly brown in color; may contain dark particles of humus.
Hemic (medium humified)	Fibrous- to cloddy-amorphous, visible fine fibres in humus; peat almost non-elastic after water extraction. Large fragments made of reed or woody remains, crushed between fingers into an amorphous mass.	Humus flowing with water or oozing between fingers and forming less than 1/3 peat mass.	In paludic sites water oozes in sparse drops or trickles down as a thick, greasy fluid darkened by humus; in drying peat sites, water is slightly colored by humus and may not be used to determine the degree of decomposition.
Sapric (highly humified)	Amorphous structure; dark, homogeneous mass sporadically interspersed with coarser plant remains. (wood, reed).	Humus oozing between fingers, comprising at least half of the peat.	Water may not be extracted from peat; mainly humus is extracted.

Fibric, Hemic and Sapric are three major classifications. **Fibric** (L. *fibra;* fibre) commonly has a bulk density of less than 0.1 g/cm^3 and a fibre content exceeding two-thirds of the volume, when saturated, ranging from about 850 percent to over 3 000 percent of the weight of oven-dried material. Its color is commonly light yellowish brown, dark brown or reddish brown.

Table 2-4 lists the Von Post's Table and the comparisons between von Post's system and the U.S. Soil Taxonomy system.

Table 2-4 Degree of decomposition of peat by theVon Post's humosity (H) grade and the US Soil Taxonomy system (Bozkurt et al., 2000; Wüst et al., 2002)

Scale number	Description	Proportion of "Dy"	Plant structure	Pressed fluid	Peat lost	Peat retained		US Soil Tax.
						Consistency	Color	
H1	Completely unhumified	None		Colorless, clear				FIBRIC Mostly sphagnum high fiber content
H2	Virtually unhumified	None		Yellow-brown clear				
H3	Little humified	Small		Noticeably turbid	None	Not porridge		
H4	Poorly humified	Modest		Very turbid	None	Somewhat porridgey		HEMIC Mostly reed-sedge Moderate fiber content
H5	Fairly humified distinct structure	Fair	Plain, but somewhat obscured	Strongly turbid	Some	Very porridgey		
H6	Fairly humified structure	Fair	Indistinct but still clear		Up to 1/3	Very porridgey		
H7	Quite well humified	Considerable	Mush still visible		About 1/2	Gruel-like	Very dark	SAPRIC Low fiber content Often high ash
H8	Well humified	Large	Vague		About 2/3	Only roots and fibrous matter remain		
H9	Almost completely humified	Most	Almost none visible		Almos t all	Homogeneous		
H10	Completely humified	All	Non visible		All	porridge		

Hemic (Gk. *hemi;* half) is intermediate in degree of decomposition. Bulk density is commonly between 0.07 g/cm^3 and 0.18 g/cm^3 and the fibre content is normally between one-third and two-thirds of the volume. The maximum water content when saturated ranges from about 450 to 850 percent. **Sapric** (Gk. *sapros;* rotten) is the most highly decomposed. Bulk density is commonly 0.2 g/cm^3 or more, and the fibre content

averages less than one-third of the volume. The maximum water content when saturated normally is less than 450 percent of the oven-dry base (FAO, 2010).

When using Von Post's Table, the classification of peat is usually determined by manually squeezing the peat: a small amount of peat is crushed in the hand, the color of the water then running out and the nature of the crushed residues allow the degree of decomposition to be determined in values of H1 to H10 according to the scale shown in **Table 2-4**. "Dy" in the table represents dry yield which is a measure of decomposed matter after drying. So when there is none, it means that after some form of drying no dry matter was obtained as in decomposed dry matter. This summary provides the information and knowledge for the classification of peat in the current experiment. The classifications shown in **Table 2-3** and **Table 2-4** are used as a reference for the classification of peat used in the current experiment, the results of which are shown in **Table 3-1**.

2.5.2 Peat as a Removal Agent for Various Contaminants

Peat has been shown by various laboratory works to be an effective sorbent for treating domestic wastewater, landfill leachate, oily contaminated water and heavy metal-contaminated water (Calkin, et al., 1976; McLellan and Rock, 1987). In recent years, this product has been increasingly used as an environmentally friendly and easily accessible commercial material (Bord Na Mona, 2001).

The relatively higher specific surface area of peat compared to other soils, is reported to be on average 200 m^2 per gram, with its lower bulk density, 0.15 – 0.25 g/cm^3

based on various types of peat. Its light weight makes peat easier to handle as a contaminant adsorbent (Bord Na Mona, 2001) compared to other materials such as rice husks and clay.

More than 109 types of bacteria per gram and its fibrous structure make peat perform like a bio-medium. Peat can effectively treat eutrophic septic wastewater as a filter due to its good hydraulic conductivity and ease of bio-degradation (Latter et al., 1967).

It has been reported that peat could adsorb oil as much as 7 times to 20 times its own weight (Bord Na Mona, 2001; Suni et al., 2004). Peat has also been used not only for the removal of TSSs, COD and BOD, but for the removal of heavy metal contaminants from mining wastewater, landfill leachate and processing wastewater (Pérez et al., 2005; Dissanayake and Weerasooriya, 1982; McLellan and Rock, 1987).

2.5.3 Peat Resources in Newfoundland

Most commercial peat moss in Canada is Sphagnum or Hypnum. Only small quantities of reed and sedge moss are harvested on a commercial basis. All exports are either Sphagnum or Hypnum (Stevenson and Kellogg Ltd., 1976). In 1990, on a volume basis, there was an estimation of three trillion cubic meters of peat deposit in Canada (Spill Sorb, 1998). By the end of 1995, Northland Associates reported that 67,771 individual peat deposits were mapped on the island of Newfoundland with a total volume of 15.2 billion cubic meters. This data includes 8.5 billion cubic meters of fuel grade peat and 6.8 billion cubic meters of horticultural-grade peat (ERC, 1995).

A survey carried out by the European Research Council (ERC) for the Newfoundland and Labrador government reported that peat was mainly used as a combustible resource, a horticultural medium and for agricultural use. However, they indicated a fourth main application of peat for special use as an absorbent, which has promising prospects (ERC, 1995).

Hi-Point Peat is a local industry manufacturing and selling peat products based on the special absorptive capacity of the Newfoundland peat (Stevenson and Kellogg, Ltd., 1976; ERC, 1995). Manufactured peat products by Hi-Point Peat have been sent to major oil companies all over the world and used on oil spill accidents such as the 1989 Exxon Valdez oil spill in Alaska, where it was proven to be very effective (NOAA/HMRAD, 1992).

2.6 Peat Applied as an Oil Sorbent

One of the advantages of using peat as an adsorbent to clean up oil spills was its properties of natural recyclability and reproducibility compared to other synthetic materials which involved higher energy consumption during manufacture. Also, its natural high adsorbing ability was another pronounced characteristic.

A study by Viraraghaven and Mathavan (1990) reported that the removal rate for standard mineral oil and crude oil from wastewater using peat reached 83% and 70%, respectively. For treating domestic wastewater with high levels of COD, BOD and SS, Perez et al. (2005) showed that two types of peat, namely sapric (most decomposed) and fibric (least decomposed) peat performed equally well in removing the SS but performed

unsatisfactorily in removing BOD and COD. On the other hand, Corley et al. (2006) reported BOD and COD removal rates by sapric and fibirc peat were as 96% and 84% respectively. For removing oil contaminants in water, Cohen et al. (1991) determined that the more humified the peat type, the better the adsorption of hydrocarbons.

Ghaly and Pyke (2001) reported that applying commercial peat to the surface of oily contaminated water resulted in an oil removal efficiency of 99.998%. A 1.3 cm thick synthetically produced oil slick was almost completely removed by sprinkling peat on the surface of the water. Coagulation was proven to be the dominant mechanism in their experiment. However, simultaneously increasing peat's moisture content would adversely affect removal because the increasing moisture content could increase peat's weight and cause the sample to sink and the procedure would have to be discontinued.

A typical peat application in the clean-up of an oil spill in Canada was reported in February 4, 1970, when the steam tanker Arrow grounded off the coast of Nova Scotia. The vessel broke into two pieces seven days after the accident and spilt 16,000 tons of bunker C oil. The harsh environment, including ice floating on the sea in that area and strong winds, enhanced the extension of the slick under the influence of tides and current towards the shore, contaminating wharves and boats. The eventual situation was reported at 300 kilometers off the shoreline where oil ranging from a trace to very heavy coverage was seen (NOAA/HMARD, 1992).

Peat was placed around the contaminated wharves and boats in order to adsorb the oil slick. It was reported that peat moss stuck to the oil effectively. After the peat mixed with the oil, it was easily removed by using a rake since they were fully combined.

However, the adsorption ability decreased when the oil interacted fully with the water forming a water-in-oil emulsion (NOAA/HMARD, 1992).

Other oil spill accidents have also been reported where peat worked effectively in removing the oil slick around the beach. As high as 95% removal efficiency was obtained when peat was applied to remove bunker C oil at the Patrick Morris sinking accident in Nova Scotia in 1970 (Spill Sorb, 1998). Similar removal efficiency was reported on rocky shorelines in 1970, in which peat was spread at a rate of 4 cubic feet per 100 square feet of beach (Spill Sorb, 1998).

The reason why peat has not been widely used in oil spills treatment might due to tough weather conditions at sea since most of large oil spill occurred in areas with strong winds, varied current directions and high waves. The removal efficiency might be greatly impacted by these negative factors.

The oil adsorbing ability of peat has been tested in the lab by spraying peat on the surface of water or using a column test. However, the combination of external conditions such as water turbulence and water temperature was lacking in previous experimental results. Unstable factors such as meteorology or water environment could have a great impact on the oil removal efficiency of peat application and could directly cause the failure of using peat. The current study considered potential water conditions that could have an effect on removal treatment and analyzed the oil adsorbing ability of peat.

2.7 Government Guidelines

There were several official regulations and limitations for Total Petroleum Hydrocarbons (TPHs) in different fields and regions. Most of them were for drinking water quality; a few of them were for discharging from industry or municipal sewerage systems. Health Canada has reported difficulties in establishing criteria for oil and grease or petroleum products in water which is for recreation, as the mixtures falling under this category are very complex. Therefore, Canadian Council of Ministers of the Environment (CCME) and Health Canada (Health Canada, 2009) suggest that oil or petrochemicals should not be present in concentrations that:

1) Can be detected as a visible film, sheen, or discoloration on the surface,

2) Can be detected by odor, and

3) Can form deposits on shoreline and bottom sediments that are detectable by sight or odor.

Based on the recommendation, using peat as a sorbent to remove oil from water can meet the first two regulations while for the third, it might be risky to use peat since contaminated peat particles could fall down to the bottom of the water body or be carried away downstream by water currents. A quick but efficient process or other filter process might be conducted while applying peat in real situations.

However, there are some clear limits and regulations at provincial levels and by some scientific studies which recommended the TPHs limitation for drinking water or inhalation. The experimental results from this research are compared with these government regulations in order to detect which level the treated water could meet in current study. A closure plan provided by the National Park Service (NPS) indicated that

the TPH in the ground water was not allowed to exceed 50 ppm (approximately equivalent to 42 mg/L based on the diesel used in the current study), while the TPH should be lower than 1000 ppm in the soil (NPS, 2003). A report from the Colomac Remediation Project – Petroleum Hydrocarbon Contaminated Water Management, Contaminants and Remediation Directorate, Indian and Northern Affairs Canada clearly indicated that 15 mg/L had been adopted as the cut-off screening for the transfer of treated water from the Oily Water Separator (OWS) to the Fish Pond and eventual discharge to the environment (INAC, 2006). This report was employed in the current study to determine the Canadian national guideline for the TPH in the water since Canadian Council of Ministers of the Environment (CCME) only provided BTEX guideline in the water, which could not completely represent the level of petroleum products in the water (CCME, 2010).

The various guidelines have different thresholds and cut-offs indicating different targets and suggesting different functions of the water bodies, e.g. portable water supply (Class I), shellfish propagation or harvesting (Class II), recreation, propagation and maintenance of a healthy, well-balanced population of fish and wildlife (Class III), agricultural water supplies (Class IV), navigation, utility and industrial use (Class V), which was derived from the Surface Water Cleanup Target Levels (SWCTLs) established in Chapter 62-302.530 of the Florida Administration Code (SLAF, 2010). This is the reason for the variation among the guidelines or limitation regulations. When comparing the different guidelines, it is helpful to point out where the peat could be used to achieve a specific goal.

Table 2-5 Governmental guidelines to oil disposal limitation

Regulation	Required TPHs value (mg/L)	Purpose of the regulation/limits	Reference
Wyoming Drinking Water Equivalent Level (DWEL)	1.1	The Wyoming DWEL for TPHs-DRO (diesel range organics) is based on protection of groundwater to drinking water quality for non-cancer effects.	LAUST Program Policy and Procedure #36 Water Quality Division, WDEQ, 2003
New Mexico Environment Department TPHs Screening Guideline (GW-1)[1]	1.72	The standard applies when groundwater may be used for drinking water purposes or based on ingestion and use of groundwater as a potable water supply.	NMED, 2006
Province of Newfoundland and Labrador Contaminated Sites Cleanup Criteria	15	Limit the discharge of oil or by-products of oil, flammable, explosive, toxic, poisonous or corrosive liquids, solids or gases and other materials. Also the limitation is suitable for the Freshwater Aquatic.	RBCA, 1997
INCA	15	Life criteria for BTEX and Lead and TPHs. Oily water remediation project	INCA, 2006
New Mexico Environment Department TPHs Screening Guideline (GW-2)[2]	30.4	The standard is based on "inhalation exposure" and only applied for the evaluation of inhalation exposure.	NMED, 2006
NPS Closure Plan	42	Scenic and recreation water environment	NPS, 2003

[1]: the regulation for drinking water;[2]: the regulation for inhalation

Table 2-5 is a summary of governmental criteria from some selected countries or regions. The difference among the TPHs was due to the different targets. For drinking water the TPH is strictly limited by the regulation, but the limitation value is relatively higher if the water is just being disposed in the river.

2.8 Software and Equipment

To determine which type of distribution the data might represent and to obtain reliable and accurate results require a large number of samples, but due to limited experimental cost, time and space, experimental design and statistical analysis can help to obtain reliable results with an optimum sample number. When several factors with varied levels (e.g. high and low levels in the current experiment) are involved in an experiment, Design Expert 7.0® could suggest a smaller number of experimental combinations while obtaining reliable and effective results before the experiment is conducted, therefore the cost, time and space could be effectively saved.

For a dissolved oil removal application, regression analysis is a strong statistical tool for detecting the relationship between a variable (that is measured, controlled or manipulated in the research; the variable is the initially dissolved oil concentration in the current experiment) and the response (subject to the variation of the variable, the response is the adsorbed oil concentration in the current experiment) when peat is applied to remove the diesel.

2.8.1 Two-level Factorial Design

Stat-Ease developed Design of Experiment (DOE) software such as Design Expert 7.0 for the design of experiments to optimize many processes. As statistical analysis software, it provides various statistical tools such as analysis of variance (ANOVA) (see **Table D-1** for ANOVA table definition, **Table D-2** for the layout of the data of the example and **Table D-3** for basic two-way ANOVA table calculation), Two-

Level Factorial screening designs and General Factorial studies. The two-level factorial design was the main statistical tool employed in the current experiment.

The Two-level factorial design is a screening model that screens many factors and identifies the vital ones that affect the process or products significantly so that a breakthrough improvement can be made based on the optimization results given by the model. The interactions between the factors are also analyzed by the model.

Figure 2-3 shows the basic procedures of analyzing data by Design Expert 7.0.

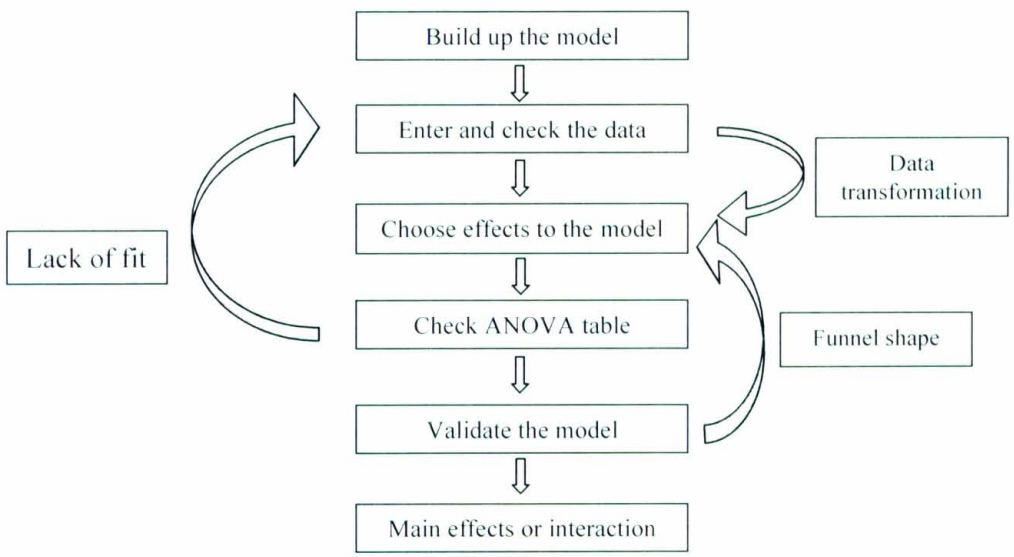


Figure 2-3 Schematic of data analyses by Design Expert 7.0 (adapted from StatEase, 2007)

1) Building up the model

The design builder offers a full and fractional two-level factorial for n factors (n is the number of factors that will be analyzed, 21>n>2) in powers of two up to 512 runs.

Fractional factorial design is devised for saving experimental time and cost within the acceptable risk range. For example, if there are five factors and two levels for each factor, there will be a total of 2^5 runs to test all combinations. To save experimental time and cost, in other words, to decrease the number of runs, Design Expert 7.0 can select out one half of all the combinations (in this case 16), while still providing an optimum solution. The lower the number of the runs is, the higher the risk of the test is. However, the Design Builder warns when a high risk model is encountered (StatEase, 2007).

2) Entering and checking data

Once the model is built up, the unit for each factor and the values of high and low levels for each factor are entered; the unit for response is entered at the same time. The ratio of the maximum to the minimum of the response (TPHs) can then be calculated. Data transformation such as square root, natural log or base ten log is suggested if the ratio is larger than ten (StatEase, 2007).

3) Choosing effects to model

An effect is the percentage of the contribution of a factor to the final response or the percentage of the contribution of each factor to the remaining TPHs in the current experiment. The effects list shows the percent contribution of each factor and the interaction among factors. The factors and interactions that contribute most to the designated model are manually selected and automatically marked as "M" indicating they are meaningful and should be modeled, while the remaining factors or interactions are

automatically marked as "E" representing those factors or interactions that should be eliminated. Checking the ANOVA table (the table containing ANOVA information) is part of the model validation. The calculated p-value, or the probability of rejecting a term that does not affect the response of the model (known as a null hypothesis, see Appendix E), should be larger than the α-value, or the probability of a small probability event (0.1 in this study), to indicate the model, terms and interaction are significant (StatEase, 2007).

4) Validating the model

The model is validated to ensure its reliability. Several plots are made to check the validation of the model (see Appendix E). Some plots are important to validate the model such as normal plots of residuals (errors), residuals versus predicted response values, residuals versus run values and predicted values versus actual values (StatEase, 2007)

5) Examining the main effects and any interaction

If the validation does not reveal any problems, the model will suggest the significant factor effects. The relationships of all factors and interactions chosen from the effect list (step 3 **Choosing factors to model**) to the final response will be shown (StatEase, 2007).

2.8.2 Regression Analysis

Regression is a technique for assessing the strength of a linear relationship existing between two variables. When conducting regression analysis in Minitab 15®, the response and variables need to be entered by the user at the data input stage. Then the regression equation and standard regression plot are automatically outputted by Minitab 15®. The regression equation is in the form $y = ax + b$, in which y is the dependent response, x is the independent variable, a is the slope and b is the intercept. This equation shows the linear relationship between the response and a variable.

2.8.3 GC-FID

Total Petroleum Hydrocarbon (TPHs) is a term used to denote a large family of several hundred chemical compounds that originally come from crude oil. The amount of TPHs found in a sample is useful as a general indicator of petroleum contamination at that site. It is better to divide TPHs into groups of petroleum hydrocarbons that act alike in the soil or water then scientists can better know what happens to them (ATSDR, 1999; EOE, 2008).

Several methods and types of equipment can be employed in TPHs analysis including Infrared Radiation (IR), Gas Chromatography (GC)/Mass Spectrometry (MS) and GC/ Flame Ionization Detector (FID). Different sample pre-treatments and analyses methods lead to different detected limits. For example, GC/MS can obtain the range of detection limit to parts per billion (ppb) (ATSDR, 2009).

In terms of petroleum-contaminated water samples, GC is important to determine individual species in most hydrocarbon-contaminated water samples. The combination

of the FID and GC is a well developed, robust and cheap procedure to fingerprint and quantitatively analyze aliphatic hydrocarbons in water or soil samples (Noudjou, et al., 2006). In the present experiment, GC-FID is used to detect larger molecules in contaminated effluent, such as n-C_{10}-n-C_{32} alkenes. Based on the cost, time and feasibility of the current experiment, GC/FID pre-treated samples were prepared in the MUN Environmental Lab including extraction (to meet the GC/FID sample requirement). GC/FID was employed and TPHs analysis was carried out in the certified laboratory of Maxxam Analytics Inc., St. John's, Newfoundland.

TPH analysis followed the guideline of Atlantic Risk Based Corrective Action (Atlantic RBCA). This guideline is for TPH analysis in water and soil samples. For the water samples in the current study, the experimental procedure followed the method for water samples by Extractable Petroleum Hydrocarbon (EPH) sample preparation (RBCA, 1999).

3 Methods and Laboratory Experiment

The laboratory experiment using peat as an adsorbent for oil removal from water was carried out in the Environmental Engineering laboratory of the Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland. Collected peat-treated water samples were analyzed in a commercial laboratory (Maxxam Analytics Inc., St. John's, Newfoundland). The experiments were conducted between January and August, 2009.

Certain information required immediately after an oil spill accident as suggested by the Freshwater Spill Information Clearinghouse is shown in **Table A-1** in Appendix A (FSIC, 2003). The required information provided a good reference for narrowing and selecting the factors used in the current experiment. According to the form, weather information such as wind speed and temperature were required. It was reported that weather factors could be dominant factors in oil spill clean-up application (Patin, 1999). Considering the laboratory condition, temperature was chosen as a factor that could have effect on remaining TPH and current was simulated by stirrer. The quality of the product was mentioned in the form indicating different clean-up approaches might be deployed based on the scale of the oil spill. Therefore, varied amount of oil spill was selected as a factor. More details on factor selection will be introduced in the **Section Experimental Factors**.

Simple preliminary tests were carried out before the batch tests in order to ensure the success of the designed experimental procedures. The determination of the two levels

of each factor was also based on the results from the preliminary tests. Thereafter, batch beaker tests were conducted to simulate oil spill accidents that could occur in natural freshwater areas. Irving commercial diesel oil was used as the source of crude oil.

Other small batch tests (8 combinations) were conducted to investigate the adsorbing ability of peat on removing dissolved oil. Experimental procedures were the same except for a few steps as mentioned in **Section Experimental Procedures**. Treated water was collected and analyzed by GC-FID to obtain TPHs.

3.1 Experimental Preparation

3.1.1 Peat

In June 2009, peat samples were obtained from the peat bog vegetation at a private farm on the Avalon Peninsula owned by Traverse Gardens at Torbay, St. John's, Newfoundland. Two types of peat were dug from the same vegetation, horticultural (poorly humified) peat and highly decomposed (highly humified) peat.

Table 3-1 Comparison between horticultural peat and highly decomposed peat

Peat characteristics	Horticultural peat	Highly decomposed peat
Color	Brown	Dark brown, almost black with fine peat particles
Composition	Peat particle coarse, a few undecomposed roots and leaves	Fewer undecomposed roots
Wet	Little water can be squeezed out	Clean water can be squeezed out
Shape	Particles were not homogeneously distributed	Almost homogenous, big sticky clumps present
von Post's level[1]	H3-H5	H7-H8

[1]: refers to classification shown in **Table 2-3**.

The peat had been carefully sealed in industrial waterproof bags and stored in the environmental lab following the instructions of the vender Ross Travers who is also a peat specialist. There was no direct sunshine in the environmental lab (no windows) and the air temperature was consistently controlled by the central air-conditioning system at 22°C, therefore, any variation of the peat characteristics due to seasonal change could be eliminated in experimental process. The physical characteristics of these peat types are listed in **Table 3-1**.

Figure 3-1 depicts the dried forms of the highly decomposed and horticultural Newfoundland peats respectively with the latter possessing less peat clumps than the former.

(a) (b)

Figure 3-1 (a) Partially dried highly decomposed peat; (b) horticultural peat

These two types of peat were homogeneously spread on six trays in the laboratory and air dried. The spread peat samples were frequently stirred (3-4 times per day) to ensure that all peat particles were completely exposed to the air. The extent of drying depended on the peat type and humidity of the samples with the highly humified peat

taking more than ten days while the horticultural peat took seven days to complete the air drying.

After drying, non-decomposed plant roots and debris were removed from both peat samples. The highly humified peat contained more clumpy particles which needed to be smashed before the air drying process. From laboratory observation, it was noted that wet peat particles tend to stick to each other and might cause errors in distribution results, therefore the smash process was necessary to break down the big clumpy particles. The air dried peats were transferred into labeled beakers covered with plastic film to avoid moisture absorption and the introduction of external particles.

The air dried peat samples were then classified into groups based on particle size range which are **> 2 mm, ≥ 300 µm** and **< 300 µm**. The debris such as vegetation roots were removed since they were not peat particles. For those peat particles size larger than 300 µm was defined as coarse peat particles and those smaller than 300 µm was defined as fine peat particle size.

3.1.2 Water and Diesel

Diesel for experimental use was bought from an Irving gas station, St. John's, Newfoundland. To test the optimum external conditions for using peat to remove diesel from water and also to simulate as natural a water environment as possible, instead of tap water or distilled water, natural lake water was collected from Quidi Vidi Lake, St. John's, Newfoundland without any treatment. No background analysis was conducted on the water samples. The water was sealed and stored in a refrigerator at 4°C in order to

avoid the introduction of external contaminants not associated with the lake. The location of Quidi Vidi Lake, which has no direct connection with sea, is shown in **Figure B-1** in Appendix B.

3.2 Experimental Procedures

3.2.1 Preliminary Tests

Preliminary tests were carried out before the final batch tests were undertaken. The aims of the preliminary tests were to: establish, if any, the contribution of the selected experimental factors on the remaining TPHs; determine the two levels of each factor; qualitatively prove the adsorbing ability of peat; and identify possible experimental adjustments to the batch tests steps.

To help understand the current experiment; the experimental design flow is shown as **Figure 3-2**.

Detailed stages corresponding to **Figure 3-2**:

A: Analysis

E: Experimental process

P: Pretreatment

P1): Peat was air dried and separated based on distribution.

E1): Diesel was added, mixed solution was stirred and peat was placed on the surface of water reacting for a certain time.

E2): Mixed product (contaminated peat and treated water) was filtered.

A1): Filtered effluent was extracted and analyzed by GC-FID.

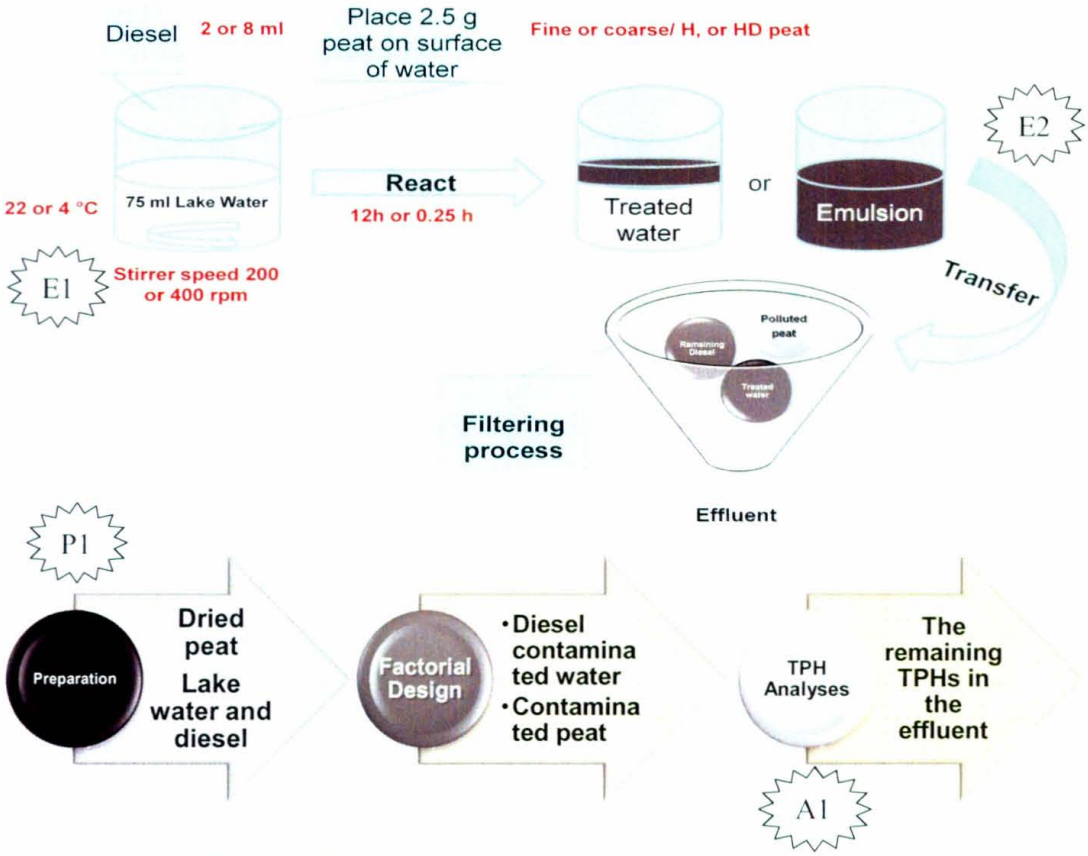


Figure 3-2 Schematic flow for current experiment

Preliminary tests procedures are as follows

1) 75 mL stored lake water (collected from Quidi Vidi Lake) was placed in a 200 mL glass beaker for each combination.

2) 8 mL or 2 mL diesel was added to the lake water by pipette (ASTM F1209-89, 1999).

3) The diesel-water mixture was stirred at 600 rpm for 0.25 h at room temperature (22 °C) by Corning PC-220 Hot Plate/Stirrer.

4) 2.5 g of the original air dried peat was placed on the surface of the water in the beaker at room temperature (22 °C). Peat was placed on the surface of contaminated water 0.25 h after adding diesel to the water. The aim of the current study was to simulate a real situation as closely as possible and test the adsorbing ability of peat in such a condition, therefore the evaporation of diesel could be discounted as a factor when compared to the complex outside meteorological and water conditions. Furthermore, the flash point of diesel is approximately 38 – 54 °C (MSDS, 2011), while the experimental temperature (22 or 4 °C) was much lower than this and hardly caused any diesel to evaporate.

5) The peat and diesel-water were in contact for 12 h with stirring at 600 rpm.

6) The contaminated peat and diesel-water solutions were filtered by self-designed filtering system to separate the peat and treated water (22 °C). See **Section Filtration System**.

7) The treated water was collected in 50 mL glass tube fitted with Teflon lined cap and stored at 4°C for TPHs extraction.

8) The TPHs was extracted (**Section TPHs Analysis**) from the effluent (treated water) using the guideline of Atlantic RBCA and collected in 2mL glass vial to be analyzed by GC-FID.

9) The TPHs in each treated water sample was analyzed by GC-FID with emphasis on the range of C_{11}-C_{32} by the guideline of Atlantic RBCA.

3.2.2 Filtration System

1) The contaminated peat and treated water were separated through a self-designed filtration system after 0.25 or 12 h contact time in the beaker. Fine Class (45 μm Fisherbrand®) filter paper was used as the filtering medium and a 50mL glass tube was used for collecting the effluent (treated water). The mixture of peat and diesel-contaminated water was carefully and gradually poured through a glass funnel. **Figure 3-3** shows the experimental set-up employed at this stage.

Figure 3-3 Filtering set

2) The contaminated peat was placed and sealed in a 2L glass jar fitted with Teflon lined cap in the shade (at 22 °C) and eventually was collected by a laboratory specialist for disposal.

3) Filter paper could somehow adsorb oil that had already adhered to peat particles or small amounts in the treated water, therefore, filter paper would be required in

a real situation if similar remaining TPH in the treated water were expected. Therefore, in a real situation, to obtain a similar TPH in the treated water, filter paper or another filtering system would be required.

3.2.3 Preliminary Test and Findings

1) An approximately 5 mm floating oil thickness could be clearly observed after 8 mL of diesel was added to the 200 mL glass beaker. Most of the diesel floated on the surface of the water with or without magnetic stirring, suggesting that diesel would float on the surface of water regardless of water turbulence in the first stage of an oil spill.

2) The floating oil adhered to the peat immediately after the peat was added. This indicated that peat performed efficiently and immediately at absorbing oil from fresh water. There was a slight difference between placing peat on the surface of still and stirred contaminated water samples over the short-term (0.25 h) test. Peat remained floating on the surface of contaminated water in the still water environment and a few peat particles could be observed suspended in the water in the stirred water environment.

3) Floating peat remained after 0.25 h of oil adsorption with the oil-contaminated peat forming a massive thick layer on the water. This observation was for both the stirred and unstirred water. There was peat emulsification during the long-term (12 h) run with fine peat particles of size < 250 mm. The effluent (treated water) from the filtration contained no oil film and no diesel odor was perceived.

3.2.4 Changes of Procedures for the Batch Tests

Slight changes were made for the batch tests based on the selection of two levels of each factor.

1) The diesel-water mixing solution was stirred at 200 rpm or 400 rpm for 0.25 h before the peat was placed on the surface of the water. The water temperature was set based on each combination at 4 °C or 22 °C (replacing step 3 in preliminary test).

2) Coarse or fine horticultural or highly decomposed peat was added based on the combination; particle size was classified based on **Table 3-2** (replacing step 4).

3) A 4 °C environment was simulated by the "ice-box" whereby the beaker containing the oil and water with the spread peat was put in a large cuboid glass tank (10L) which was filled with ice cubes. A thermometer was inserted to monitor and maintain the water temperature at 4 °C. This change was to provide a constant experimental environment for combinations containing a low level of water temperature. **Figure 3-4** shows the set up.

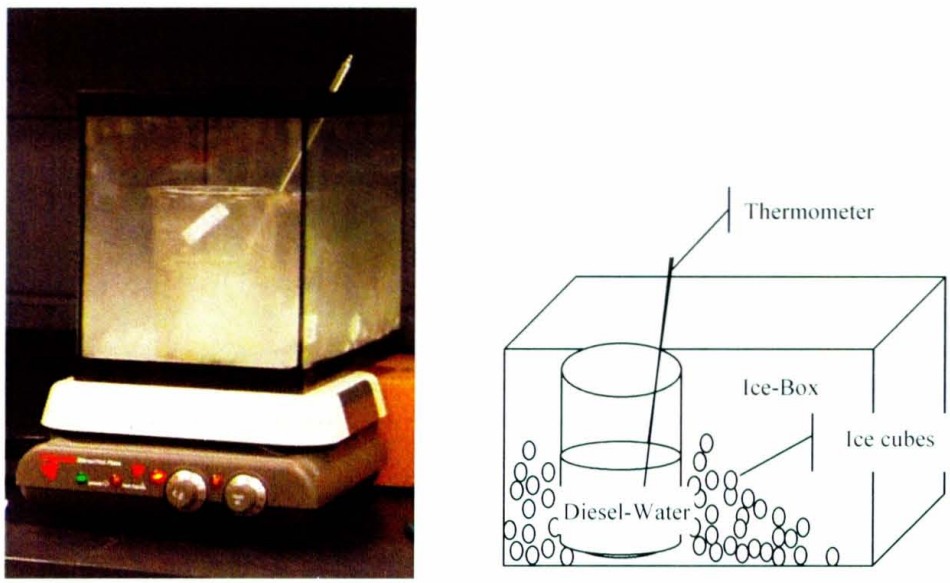


Figure 3-4 Ice-box and schematic

3.3 Experimental Factors and Choice of Levels for Factors

Based on the observation and results from the preliminary test, the levels of each factor were determined as shown in **Table 3-2**. Peat particle size is classified by category

Table 3-2 Factors and levels in Factorial Design of experiment

Factors	Level of factors	
Water temp. (°C)	22	High
	4	Low
Magnetic stirrer speed (rpm)	400	High
	200	Low
Oil volume (mL)	8	High
	2	Low
Reaction time (h)	12	High
	0.25	Low
Peat particle size	Coarse (≥ 300 μm)[1] Fine (< 300 μm)	Categorical[2]

[1]: The peat particles larger than 2 mm were removed.
[2]: Peat particle size was entered as categorical factor.

but not numerically when entering data in to the model. Due to limited knowledge, experimental costs, and time, the current experiment was only conducted in the laboratory. The results could not be extrapolated to a large-scale oil spill in a real situation, which will be required for future work.

1) **Water temperature:** The low level (4°C) was selected to simulate cold weather conditions experienced during the winter while the high level (22°C) was chosen to simulate warm weather conditions as experienced during the summer.

2) **Volume of oil:** From preliminary tests, 2 mL of diesel oil was used to represent a small-scale oil spill while 8 mL was used to simulate a large-scale oil spill. The mass of peat used was kept constant at 2.5g for each combination of volumes tested.

3) **Stirrer speed:** The high magnetic level was chosen at 400 rpm while the low level was at 200 rpm (considering there is no absolutely "still" water environment in real situation). The high level represents turbulent conditions in the river or estuary while the low level represents calm or relatively still water.

4) **Particle size:** The particle sizes were grouped into low and high with the low indicating particle sizes less than 300 μm which were fine particles (peat particles hardly identified by naked eye), while those greater than 300 μm were classified as high and were coarse in appearance. This choice was made to investigate the impact of the surface area on the adsorption capacity.

5) **Peat reaction time:** This was selected to determine the impact of the time on the spilt oil. High reaction time means 12 h after the oil spill has occurred while low reaction time implies 0.25 h after the oil spill has occurred.

6) **Peat type:** Two types of peat were used. The comparison between these categorical levels would indicate the performance of the peat types on oil removal.

3.4 Initially Dissolved Oil Test

Diesel removal efficiency has been reported to be as high as 99% (Suni et al., 2004). However, the remaining 1% was somehow more important than the 99%. When petroleum fractions entered the water body, PAHs, which are extremely harmful and toxic for aquatic plants and animals, could be derived from dissolved petroleum fractions under certain conditions. Removing the dissolved diesel was a critical task in this experiment.

The initially dissolved oil tests were a set of individual small batch tests (eight combinations included) and were aimed at showing how much diesel initially dissolved into the water before peat was added. Since peat was effective at removing most of the floating oil on the surface of the water in the preliminary test, the aim of the tests was to investigate if peat would be able to adsorb dissolved oil, believed to be the most difficult scenario in a real oil spill removal situation. The difference between the initially dissolved oil concentration and the remaining TPHs after applying peat would show the removal efficiency for dissolved oil. Certain combinations were designed to conduct the tests in order to cover all possibilities; these are summarized in **Table 3-3**.

The experimental procedures of the initially dissolved oil tests were the same as the batch tests steps except for the steps after placing peat on the surface of water. The diesel-water solution was stirred at different rpm for 0.25 h with the speeds of stirring, oil amounts and water temperatures, as shown in **Table 3-3**. The amount of diesel-contaminated water taken from the middle part of the flask by a pipette was such that >10 mL of it ensured that TPHs could be detected by GC-FID and that the sample was taken from completely below the oil film. The samples were transferred to 50 mL glass tubes fitted with Teflon caps stored at 4°C to be analyzed. No duplicates were conducted due to the experimental cost. The results and regression analysis for the initially dissolved diesel tests are as shown in **Figure 4-11** and **Table 4-8**.

Table 3-3 Experimental combinations for Initial Dissolved oil

Combination	Oil Volume (mL)	Water Temperature (°C)	Stirrer Speed (rpm)
D1	2	4	200
D2	2	4	400
D3	2	22	200
D4	2	22	400
D5	8	4	200
D6	8	4	400
D7	8	22	200
D8	8	22	400

3.5 TPHs Analysis

The TPH fraction was extracted from the effluent after the filtration process. The extraction process was conducted as instructed by Maxxam Analytics Inc. St. John's, Newfoundland and as referenced by RBCA, 1999.

1) All oil contaminated effluents were transferred to a 250 mL bottle covered with a Teflon cap.

2) The contaminated effluent was weighed and its weight was recorded.

3) Distilled water was added until to fill the bottle to 250 mL.

4) 0.1 mL internal standard was added.

5) 2 mL of hexane was added.

6) The bottle was shaken for 2 h.

7) Once the hexane had floated to the top of the 250 mL bottle, the middle layer of the hexane was extracted to ensure that there was no water. The extracted hexane was transferred to a 2 mL labeled vial.

8) A little (just enough to cover the bottom of the vial) anhydrous sodium sulfate (Na_2SO_4) was added to eliminate any water in the 2 mL vial.

9) All the 2 mL vials were labeled and automatically analyzed by GC-FID.

3.6 Data Analysis

3.6.1 Design Expert 7.0®

Design Expert 7.0® was employed to analyze the data in the current experiment following the steps listed below:

1) Building up the model

Four numeric factors (water temperature, stirrer speed, reaction time and oil volume) and two categorical factors (peat type and peat particle size) with two levels for each factor were involved in the model. To save cost and time, a two-level fractional factorial design was employed. Thirty-two (2^5) combinations were automatically determined by the model and responses (the remaining TPHs) were entered in the model.

2) Entering and checking data

Units for each factor and response were entered as well. The ratio of the maximum to the minimum of the response (TPHs) was then calculated. Data transformation such as square root, natural log or base ten log was suggested if the ratio was larger than ten (StatEase, 2007). The transformation based on Napierian Logarithms was conducted since both ratios were very close to ten.

3) Choosing effects to model

The effects list and ANOVA table (detailed calculation of the ANOVA table is shown in **Table D-1** in Appendix D) were checked and the factors which could make significant contributions to the final response were selected.

4) Validating the model

Four important plots (**Figure E-1** for highly decomposed peat and **Figure E-2** for horticultural peat in Appendix E) were checked for validating the reliability of the model. Detailed plot check information is shown in Appendix E.

3.6.2 Minitab 15®

In the current experiment, the relationship between adsorbed oil concentration and initially dissolved oil concentration were entered in Minitab 15® as response and variable. The model output showed the equation describing the linear relationship as:

Ads. = a Ini. + b, in which a was the slope and b was the intercept, Ini. was the initially dissolved oil concentration and Ads. was the adsorbed oil concentration.

4 Results and Discussion

4.1 Peat separation

Table 4-1 shows the distribution of peat separation based on the particle size range (that was obtained after the clumps in the air dried peat had been smashed).

Table 4-1 Peat particle size distribution

Particle size range	Highly decomposed peat (wt%)	Horticultural peat (wt%)
Coarse		
> 2 mm	78.5	57.2
> 850 µm	9.2	13.8
> 425 µm	4.5	13.3
> 300 µm	1.8	5.4
Fine		
> 250 µm	0.5	2.0
> 150 µm	4.1	4.4
> 75 µm	0.9	2.9
< 75 µm	0.5	1.1
Total	100	100

A test within Minitab 15® showed that the two groups of data collected for the samples had no significant difference (at 90% confident interval, neither estimated difference was zero and both p-values were larger than 0.1), which indicated the reliability of the separation. See **Appendix F** for method details.

The decomposition degree of highly decomposed peat was larger than horticultural peat (poorly humified peat), which explains why the fine particle percentage of highly decomposed peat was higher than horticultural peat in the table. The difference between particle sizes might have different effect on the concentration of remaining TPH in the treated water.

4.2 Batch Test Results

The batch tests results as shown in **Table 4-2** were first compared with the government regulations shown in **Table 2-5** and **Figure 4-1** in order to ascertain the level of removal of oil if peat is used as the sole adsorbent in the clean-up treatment.

Table 4-2 Batch tests results - the remaining TPHs in treated wastewater effluents

No.	Peat type	Reaction time (h)	Stirrer speed (rpm)	Temp. (°C)	Volume (mL)	Particle size	Average TPHs (mg/L) [1]
1	H	0.25	200	4	8	Fine	0.90
2	H	0.25	200	22	2	Fine	2.12
3	H	12	200	4	2	Fine	2.55
4	H	12	200	22	8	Fine	4.45
5	H	0.25	400	4	2	Fine	1.65
6	H	0.25	400	22	8	Fine	2.15
7[E]	H	12	400	4	8	Fine	3.35
8[E]	H	12	400	22	2	Fine	5.00
9	H	0.25	200	4	2	Coarse	3.55
10	H	0.25	200	22	8	Coarse	4.80
11	H	12	200	4	8	Coarse	2.30
12	H	12	200	22	2	Coarse	4.45
13	H	0.25	400	4	8	Coarse	3.36
14	H	0.25	400	22	2	Coarse	3.34
15[E]	H	12	400	4	2	Coarse	4.14
16[E]	H	12	400	22	8	Coarse	4.12
17	HD	0.25	200	4	8	Fine	1.63
18	HD	0.25	200	22	2	Fine	1.68
19	HD	12	200	4	2	Fine	3.30
20	HD	12	200	22	8	Fine	3.92
21	HD	0.25	400	4	2	Fine	2.85
22	HD	0.25	400	22	8	Fine	4.00
23[E]	HD	12	400	4	8	Fine	5.30
24	HD	12	400	22	2	Fine	5.65
25	HD	0.25	200	4	2	Coarse	4.82
26	HD	0.25	200	22	8	Coarse	1.23
27	HD	12	200	4	8	Coarse	2.16
28	HD	12	200	22	2	Coarse	2.23
29	HD	0.25	400	4	8	Coarse	3.53
30	HD	0.25	400	22	2	Coarse	3.92
31[E]	HD	12	400	4	2	Coarse	2.95
32[E]	HD	12	400	22	8	Coarse	4.05

[1]: The TPHs is the average of original and duplication, see TPHs values in **Table C-1** in Appendix C.
[E]: Emulsification was observed after 0.25 or 12 h reaction.

Detailed explanation based on the classification of highly decomposed peat and horticultural peat will be given in the following **Section Batch Test Analysis**. The results from the initially dissolved oil tests were then analyzed by regression analysis. The data obtained were analyzed to establish the conditions of optimum performance during the investigation.

All combinations are as proposed by Design Expert 7.0® during the design of the experiment. Two-Level Factorial Analysis and GC-FID were employed to analyze the TPHs in the treated water. The selected parameters are: Peat type (H as Horticultural peat and HD as Highly Decomposed peat); Reaction Time (0.25 h as short-term and 12 h as long-term); Stirrer speed (200 rpm as still and 400 rpm as rapid); Water Temperature (4°C as cold water environment and 22°C as high water temperature area); applied diesel Volume (2 mL for small-scale oil spill and 8 mL for large oil spills); and particle size (coarse, > 300 μm, and fine, < 300 μm).

Each TPHs value is the average of the original and duplication for each combination as shown in **Table C-1** in Appendix C. Emulsification was observed for some combinations and marked as [E] in the table.

4.3 Comparison Between Experimental Results, Government Criteria and a Related Study

To address one of the aims of the current study, that is, which level of the regulation the treated water from the current study could meet, **Figure 4-1** shows the comparison between some selected government guidelines and experimental results (government

guidelines are summarized in **Table 2-5**). The variation in the regulations was due to the different functions of the target water bodies. A drinking water resource is one of the water bodies that is critically related to human health, therefore the TPH regulation was determined as very low, while for those water bodies used for recreation or as part of the scenery the TPH level could be higher, however direct contact with such water bodies might be detrimental to the health of human beings.

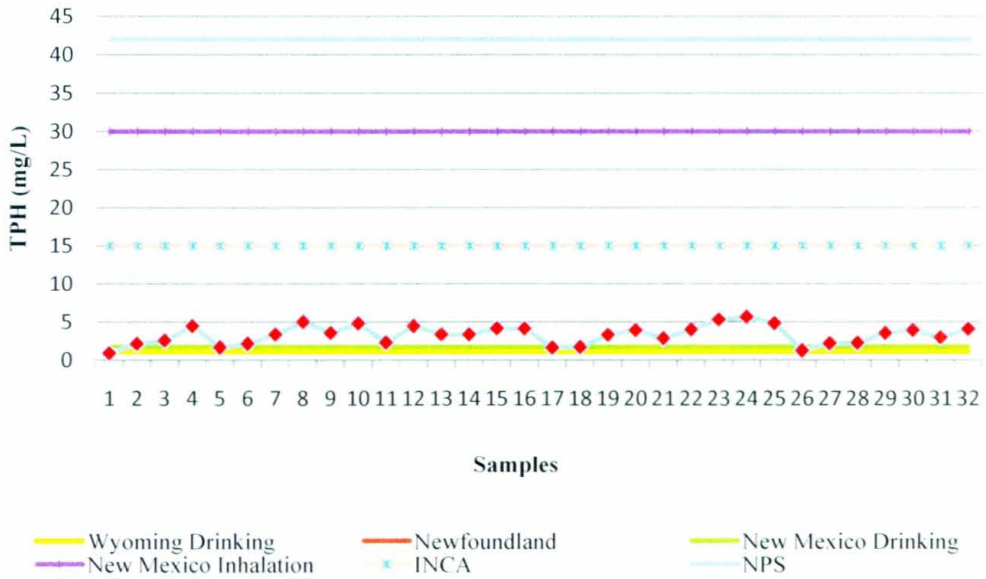


Figure 4-1 Comparison between experimental results and government guidelines

According to the plot, oil-contaminated water treated with peat hardly met drinking water conditions in New Mexico (1.17 mg/L) and Wyoming (1.1 mg/L). However, all the samples met the regulations for Newfoundland wastewater discharge (15 mg/L), which shows the high oil removal efficiency of peat from freshwater with

minimal cost from this study. If peat was used for removing oil from a natural water body, the treated water would largely be harmless for inhalation from the comparison between experimental results and the New Mexico inhalation limit (30.4 mg/L). For clean-up crews or people working around a contaminated site, the risk of inhaling harmful gas or material is significantly minimized when peat is applied on the surface of contaminated water. Although further treatment may still be required, the emergency treatment as provi-ded by peat sorption could go a long a way in saving lives, cost and time allowing the application of further effective clean-up strategies, if any.

4.4 Batch Test Analysis

The analysis of the oil removal efficiency of peat followed the route suggested by Design Expert 7.0® for 2 Level Factorial Design. Minitab 15® was also employed as a support method to this approach.

4.4.1 Highly Decomposed Peat

Data from the experiment using the highly decomposed peat were analyzed using Design Expert 7.0® in order to investigate which of the factors would have a significant effect on removing TPHs and to identify and quantify the interactions between the selected factors. The data input window is shown in **Table 4-3**.

Table 4-3 Data input for ANOVA of highly decomposed peat (modified from Design Expert 7.0®)

No.	Factor 1 A: Reaction Time	Factor 2 B: Stirrer speed	Factor 3 C: Temperature	Factor 4 D: Oil Volume	Factor 5 E: Particle Size	Response 1 TPHs
1	0.25	200	4	2	Coarse	3.44
2	0.25	200	4	2	Coarse	6.20
3	12	200	4	2	Fine	4.60
4	12	200	4	2	Fine	2.00
5	0.25	400	4	2	Fine	4.20
6	0.25	400	4	2	Fine	1.50
7	12	400	4	2	Coarse	2.30
8	12	400	4	2	Coarse	3.60
9	0.25	200	22	2	Fine	1.45
10	0.25	200	22	2	Fine	1.90
11	12	200	22	2	Coarse	1.45
12	12	200	22	2	Coarse	3.00
13	0.25	400	22	2	Coarse	3.94
14	0.25	400	22	2	Coarse	3.90
15	12	400	22	2	Fine	8.10
16	12	400	22	2	Fine	3.20
17	0.25	200	4	8	Fine	0.82
18	0.25	200	4	8	Fine	2.44
19	12	200	4	8	Coarse	2.12
20	12	200	4	8	Coarse	2.20
21	0.25	400	4	8	Coarse	4.50
22	0.25	400	4	8	Coarse	2.56
23	12	400	4	8	Fine	5.80
24	12	400	4	8	Fine	4.80
25	0.25	200	22	8	Coarse	1.17
26	0.25	200	22	8	Coarse	1.28
27	12	200	22	8	Fine	5.60
28	12	200	22	8	Fine	2.24
29	0.25	400	22	8	Fine	2.70
30	0.25	400	22	8	Fine	5.30
31	12	400	22	8	Coarse	5.20
32	12	400	22	8	Coarse	2.90

The data were analyzed using the method of ANOVA (see **Table D-4** in Appendix D). The effects of the factors and the interactions between them as investigated

in the experiment are given in **Table 4-4**. The effects list gives the contribution percentage of each factor and interaction among two factors. Therefore, the interaction among three and more factors was eliminated by the model and the total contribution in the table is not 100%. The effects list shows the contribution of each factor and interaction; a relatively large contribution could possibly be selected by the model to conduct further analysis. The same applies for **Table 4-6**.

From the list of effects, factor A - reaction time (10.31), factor B - stirrer speed (29.7) and the interaction between reaction time and particle size (interaction AE, 7.65) were the three top significant contributors to the overall response - the remaining TPHs. "M" indicates those factors that were meaningful and were to be further modeled or analyzed (involving ANOVA and model validation, etc.), while "E" indicates the factors and interactions that could be eliminated from any further analysis.

Table 4-4 The effects list of highly decomposed peat (modified from Design Expert 7.0®)

Model	Term	% Contribution
M	A-Reaction time	10.31
M	B-Stirrer speed	29.7
E	C-Water Temp.	0.19
E	D-Oil Volume	0.012
M	E-Particle Size	1.72
E	AB	1.56
E	AC	0.18
E	AD	1.84
M	AE	7.65
E	BC	2.45
E	BD	2.83
E	BE	0.015
E	CD	0.012
E	CE	2.04
E	DE	2.19

For significant factors A and B, **Figure 4-2** shows the one-factor effect on the remaining TPHs in the treated effluent.

(a)

(b)

Figure 4-2 One-factor effect - (a) reaction time and (b) stirrer speed on the remaining TPHs in the effluent for highly decomposed peat (adapted from Design Expert 7.0®)

According to these two plots, the remaining TPHs increased with reaction time for **Figure 4-2** (a) and stirrer speed for **Figure 4-2** (b). The reason might be that longer reaction time and/or turbulence caused adsorbed diesel to be released to the water from

peat particles after the initial adsorption. Therefore, if reaction time only was considered, or stirrer speed as a single factor, lower remaining TPHs in the water would be reached in a shorter reaction time and at lower water turbulence (lower stirrer speed).

Figure 4-2 also shows that reaction time and stirrer speed were two factors that contributed to the remaining TPH significantly when considered on their own. Peat particles did not perform as an integral piece like other sorbents such as polypropylene or activated carbon. The basic mechanism of peat adsorption was the reaction between the functional groups on the surface of each peat particle and the functional groups in the oil droplets. Reaction time and water turbulence were two basic factors that could largely disperse peat particles and make them lose adsorbing ability. This might be the reason why reaction time was the significant factor for horticultural peat as well (see **Figure 4-6**).

The interaction shown in **Figure 4-3** is more important to study than the one-factor analyses since it was easy to be ignored when factorial analysis conducted. According to the line marked by the triangle (**Figure 4-3**), as reaction time was increased, the adsorbing ability of coarse highly decomposed peat remained nearly constant; however a short time was desirable since longer time could cost too much. The increasing trend of the line marked with a square indicates that a short-term (0.25 h) application is preferable for fine highly decomposed peat, since the lower end of this line corresponds to the short reaction time (0.25 h as X-axis) and lowers the remaining TPHs in the water (Y-axis). The longer the time involved the greater would be the amount of TPHs re-exchanged into the treated effluent. In the real situation, short treatment time (relatively high removal rate as premise) is always expected to save cost, labor and time. Another important view is that shorter treatment time suggests shorter contact time

between contaminants and the environment so that the damage could be reduced. Therefore fine peat is recommended in this scenario.

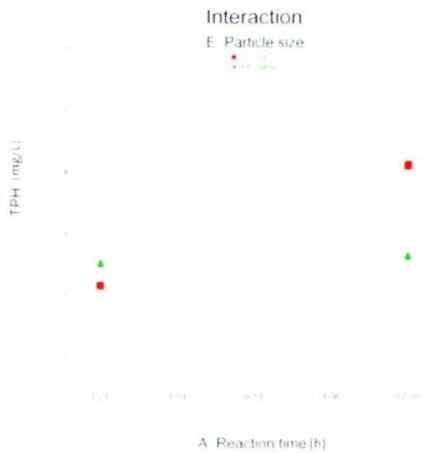
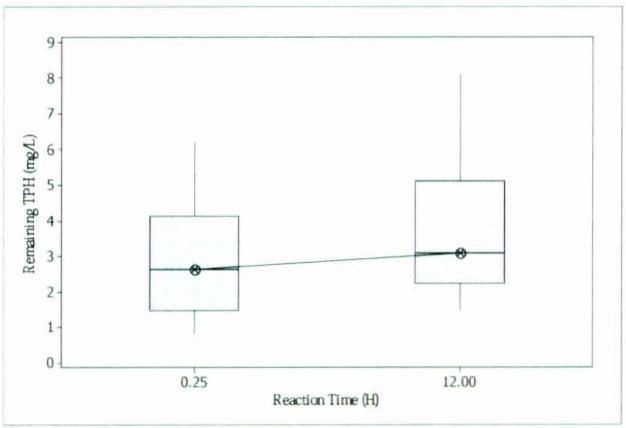


Figure 4-3 Effects of interaction among two factors on the remaining TPHs in the effluent for the highly decomposed peat (adapted from Design Expert 7.0®)

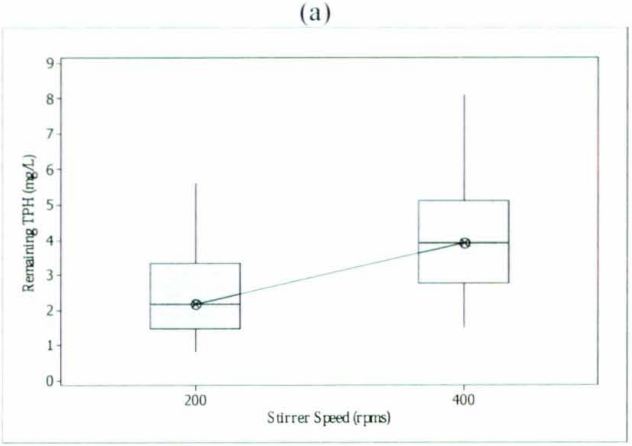
The lowest TPHs point (lower end of the square-marked line) matched the short reaction time and fine particle size of highly decomposed peat. However, there was not much difference between this combination and the short-time contact with coarse highly decomposed peat (left end of triangular marked line). The intersection point of the two lines suggests that if peat was used in a large-scale application without the pre-separation process (1:1 mixture in volume of two types of peat), approximately one fourth of the total reaction time (3 h) would be needed to complete the whole process in order to get the minimum remaining TPHs value in the treated water environment.

Figure 4-4 obtained by the use of Minitab software as an alternate method of data analysis, supports the results of the one-factor analysis from the Design Expert 7.0®. The boxpolt shows the distribution of the data and also the comparison between groups of data

by the defined classification. The vertical line in the boxplot represents the range of the data, the upper line in rectangle represents the Q3 (upper quartile, the median of the upper half of a set of data), the middle line represents the median and the bottom line represents Q1 (lower quartile, the median of the lower half of a set of data). The star represents median value while the median connecting line represents the trend between the medians.



(a)



(b)

Figure 4-4 Boxplot of the remaining TPHs by (a) reaction time and (b) stirrer speed for highly decomposed peat

Note: A cross within a circle represents the median value of the set of the data.

Figure 4-4 (a) shows that the remaining TPHs value increased with a longer reaction time and **Figure 4-4** (b) indicates that a higher concentration of TPHs remained in the effluent with higher water turbulence (stirrer speed). Both plots obtained indicate the same conclusion as with the Design Expert 7.0® (shown as **Figure 4-2**).

The minimum remaining TPHs concentration was obtained by applying fine highly decomposed peat for 0.25 h, with the maximum TPHs concentration resulting from using fine peat for 12 h. **Figure 4-5** from Minitab software also supports the interaction relationship between particle size and reaction time as suggested by Design Expert 7.0®.

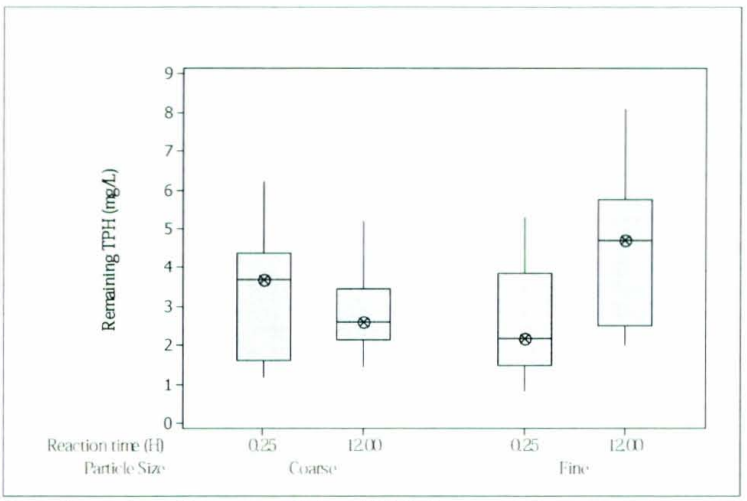


Figure 4-5 Boxplot of the remaining TPHs by particle size and reaction time for highly decomposed peat

The effect of the interaction on the response (remaining TPH) might be different from the effect on remaining TPH when only considering a single factor. For example, **Figure 4-5** shows the interaction relationship between two factors (particle size and reaction time) and the response (remaining TPH) for highly decomposed peat. It shows that for coarse highly decomposed peat, a 12 h reaction time obtains less remaining TPH in the treated

water and for fine particle sized peat a 0.25 h reaction time could obtain less remaining TPH. When just considering **Figure 4-2** or **Figure 4-4**, it appears that there is less remaining TPH only with a shorter reaction time (0.25 h). This is because **Figure 4-2** and**Figure 4-4** just suggest the relationship between the response (remaining TPH) and reaction time because only reaction time was considered; the peat was not separated into fine and coarse particles for these two figures. When peat was divided into fine and coarse it appears that fine peat might be the dominant process since the trend for the fine peat (less remaining TPH was obtained with shorter reaction time) was similar to the trend appearing in **Figure 4-3** and **Figure 4-5**. Coarse peat has less specific surface area which might explain why a longer reaction time is needed to obtain less remaining TPH. Oil might be adsorbed immediately by peat particles or adhere to peat particle surfaces right after the reaction has started, which might be the reason why fine peat needs less time to obtain less remaining TPH (Asadi, 2009). A similar explanation could be given for the comparison between **Figure 4-9** and **Figure 4-6**.

4.4.2 Horticultural Peat

The input data for Design Expert 7.0® of horticultural peat are shown in **Table 4-5**. The ANOVA table for horticultural peat is shown in **Table D-5** in Appendix D.

Table 4-5 Data input for ANOVA of horticultural peat (modified from Design Expert 7.0®)

No	Factor 1 A: Reaction Time	Factor 2 B: Stirrer speed	Factor 3 C: Temperature	Factor 4 D: Oil Volume	Factor 5 E: Particle Size	Response 1 TPHs
1	0.25	200	4	2	Coarse	2.50
2	0.25	200	22	8	Coarse	2.90
3	0.25	400	4	8	Coarse	1.62
4	0.25	400	22	2	Coarse	1.77
5	12	200	4	8	Coarse	1.18
6	12	200	22	2	Coarse	1.70
7	12	400	4	2	Coarse	2.50
8	12	400	22	8	Coarse	1.64
9	0.25	400	4	2	Fine	1.38
10	0.25	400	22	8	Fine	2.40
11	0.25	200	4	8	Fine	0.96
12	0.25	200	22	2	Fine	2.25
13	12	400	4	8	Fine	2.80
14	12	400	22	2	Fine	6.90
15	12	200	4	2	Fine	3.20
16	12	200	22	8	Fine	7.00
17	0.25	200	4	2	Coarse	4.60
18	0.25	200	22	8	Coarse	6.70
19	0.25	400	4	8	Coarse	5.10
20	0.25	400	22	2	Coarse	4.90
21	12	200	4	8	Coarse	3.41
22	12	200	22	2	Coarse	7.20
23	12	400	4	2	Coarse	5.78
24	12	400	22	8	Coarse	6.60
25	0.25	400	4	2	Fine	1.91
26	0.25	400	22	8	Fine	1.90
27	0.25	200	4	8	Fine	0.84
28	0.25	200	22	2	Fine	1.98
29	12	400	4	8	Fine	3.90
30	12	400	22	2	Fine	3.10
31	12	200	4	2	Fine	1.90
32	12	200	22	8	Fine	1.90

According to **Table 4-6**, factor A- reaction time (7.88), factor C – water temperature (7.19), factor E – particle size (6.93) and the interaction between reaction time and particle size (interaction of AE, 12.78) significantly contributed to the final response – the remaining TPHs. Compared with **Table 4-4**, the different percentage and

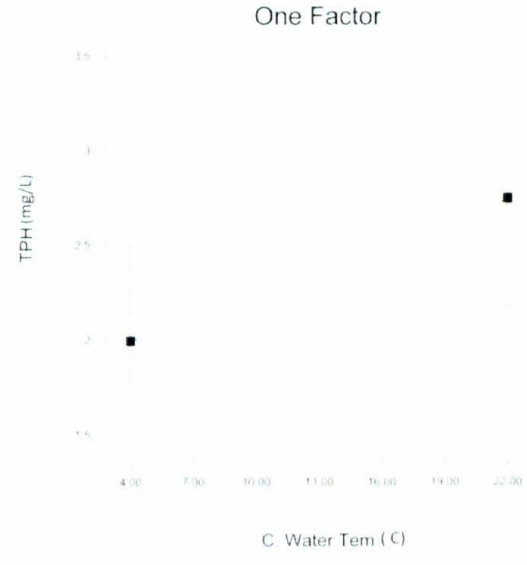
type of the contributions of the factors might be due to different functional groups on the peat particles or different chemical reactions between the two types of peat and oil droplets. "M" indicates those factors that were meaningful and were to be further modeled or analyzed (involving ANOVA and model validation, etc.), while "E" indicates the factors and interactions that could be eliminated from any further analysis.

Table 4-6 The effects list of horticultural peat (modified from Design Expert 7.0®)

Model	Term	% Contribution
M	A-Reaction time	7.88
E	B-Stirrer speed	1.44
M	C-Water Temp.	7.19
E	D-Oil Volume	1.08
M	E-Particle Size	6.93
E	AB	1.27
E	AC	0.084
E	AD	0.1
M	AE	12.78
E	BC	2.73
E	BD	0.31
E	BE	1.39
E	CD	1.64
E	CE	1.48
E	DE	0.0004

Figure 4-6 shows the one-factor effect on the remaining TPHs in the effluent treated by horticultural peat. An increasing remaining TPHs concentration with longer reaction time (**Figure 4-6**a) or higher water temperature (**Figure 4-6**b) suggests that less TPHs would remain in final effluent and more would be adsorbed by the peat at lower water temperature and shorter reaction time. In the real situation, better oil removal efficiency could be obtained with lower water temperature (4 °C) or shorter time (0.25 h) if horticultrual peat was used based on the suggestion from the model results.

(a)



(b)

Figure 4-6 One-factor effect - (a) reaction time and (b) water temperature on the remaining TPHs in the effluent for horticultural peat (adapted from Design Expert 7.0®)

Based on the theory of the reaction between peat particles and oil droplets, reaction time was determined to be one of the significant factors. Also, diesel solubility increases as the water temperature rises (Yang et al., 1997). This might be the reason for the significant factor of water temperature when horticultural peat was applied. However, future studies on this particular phenomenon or modeled results need to be conducted.

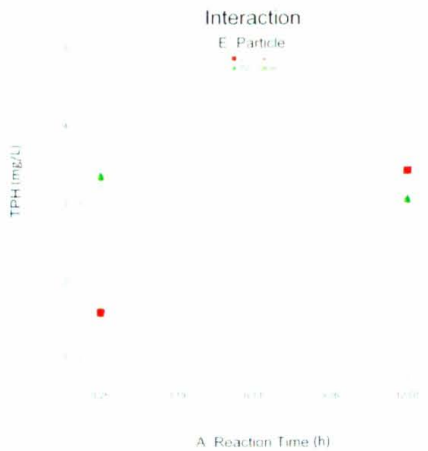


Figure 4-7 Effects of interaction among two factors on the remaining TPHs in the effluent for the horticultural peat (adapted from Design Expert 7.0®)

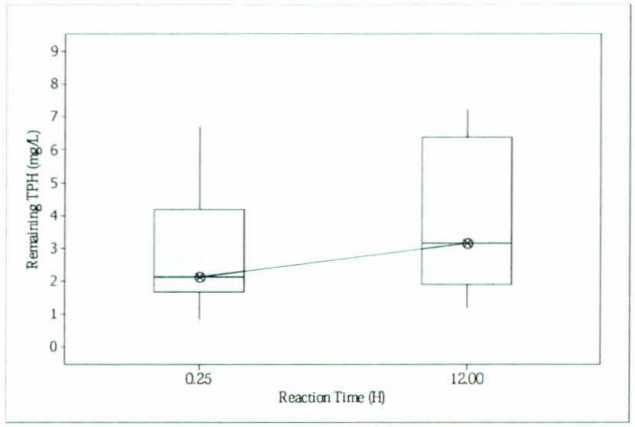
In **Figure 4-7**, the line marked by the triangle represents coarse horticultural peat, in which TPHs slightly decreased with increasing reaction time. This suggests using coarse horticultural peat would obtain almost the same remaining TPHs in the effluent regardless of time. In this case, a shorter time was greatly preferable since time and cost would be saved. Short-term application of fine horticultural peat was preferable, shown as the lower end of the square-marked line. The lowest point of the remaining TPHs value matched with short reaction time and fine particle size indicating that applying fine

horticultural peat on contaminated water for 0.25 h would obtain the minimum remaining TPHs in treated water.

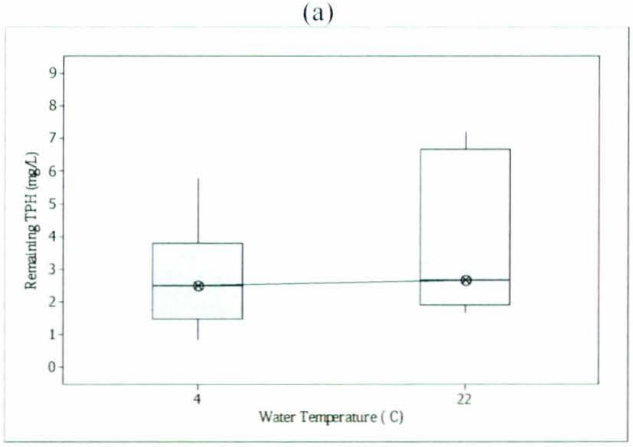
The intersection point (**Figure 4-7**) of these two lines shows that if mixed fine and coarse particle sizes of horticultural peat were used, approximately 10 h (X axis was 10 h at the intersection point) of application would be required in order to obtain a relatively ideal minimum remaining TPHs. Adding more fine horticultural peat to the mixed peat might obtain lower remaining TPHs with shorter time since the square-marked line goes down at the left-hand side of the intersection.

When compared to the three-hour optimum application (shown in **Figure 4-3**) when using mixed highly decomposed peat, the application would take longer when using horticultural peat. In order to save cost and time in a practical situation, pre-separation of peat based on particle size might be unnecessary since highly decomposed mixed peat took a shorter reaction time and as such would be a preferable clean-up material.

Figure 4-8 supports the results from Design Expert 7.0® by using Minitab 15®, an alternative method to analyze the data. **Figure 4-8** (a) shows the increasing remaining TPHs values with longer reaction time regardless of the various contributions from other factors. **Figure 4-8** (b) indicates the higher concentration of the remaining TPHs in treated water was due to higher water temperature if only water temperature was considered. Both plots lead to the same conclusion as from Design Expert 7.0® (shown as **Figure 4-6**).



(a)



(b)

Figure 4-8 Boxplot of the remaining TPHs by (a) reaction time and (b) water temperature for horticultural peat

Figure 4-9 also proves the interaction relationship between particle size and reaction time for horticultural peat. The minimum remaining TPHs concentration was obtained by applying fine horticultural peat for 0.25 h, with the maximum TPHs concentration resulting from using coarse peat for 0.25 h. An explanation for the different trends between **Figure 4-8** and **Figure 4-5** is given in the first paragraph after **Figure 4-4**.

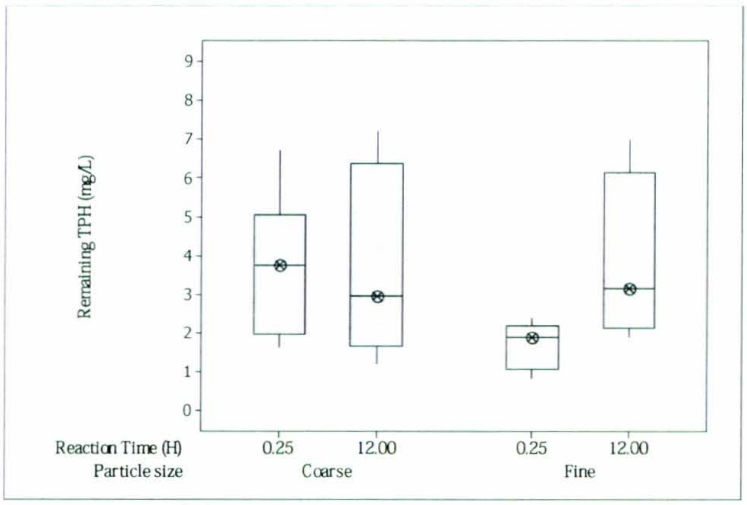


Figure 4-9 Boxplot of the remaining TPHs by reaction time and particle size for horticultural peat

4.5 Oil Removal Efficiency

This section explains the results obtained from the initially dissolved oil test. The removal efficiency for each combination is shown in **Table 4-7**. The remaining TPHs from **Table 4-7** were directly from batch TPHs analyses, the initially dissolved oil concentrations were from the initially dissolved oil test, corresponding to eight combinations from **Table 3-3, (**the 32 combinations in **Table 4-7** were derived from eight combinations in **Table 3-3** after two levels of reaction time and particle size were introduced). Removal efficiency was the ratio of the adsorbed oil concentration and initially dissolved oil concentration.

The average remaining TPHs after applying peat for all combinations was as low as 3.30 mg/L, while the overall average oil removal efficiency was as high as 99.99% (average diesel density as 0.84 g/mL at 25°C referred from IEA, 2004). Based on the data provided by Environmental Canada, the solubility of Irving automotive diesel in the

water was negligible comparing to diesel concentration (Environmental Canada, 2008). Considering the diesel concentration in the water before applying peat was 0.84 g/mL, and the average remaining TPH in the water for all combinations was 3.3 mg/L (**Table 4-7**), removal efficiency of 99.99% could then be obtained using the following equation (**Eq. 4-1**). Laboratory tests or experiments using peat for oil removal applications have produced different levels of efficiency (see **Table 4-9** for the comparison among applications). The level of oil recovery using peat varies according to different external conditions such as extreme weather (e.g. strong winds) and strong water energy (e.g. strong waves). The current experimental results were close to those from the tests by Ghaly et al. (2001), which might be due to the similar experimental apparatus.

$$Removal\ Efficiency = \frac{Diesel\ conc.before\ applying\ peat - average\ remaining\ TPH}{Diesel\ conc.\ before\ applying\ peat}$$

Eq. 4-1 Removal efficiency of peat

Dissolved oil was believed to be one of the most difficult proportions to clean up after an oil spill accident. The experiment was based on the assumption that most of the floating oil was removed by the peat since there was no visible oil film and no odor could be detected. Thereafter, the adsorbing ability of removing dissolved oil was tested. Results showed that most dissolved oil was efficiently removed by peat and the average efficiency was 77.21% (all experimental results in this paragraph refer to **Table 4-7**). This value also indicates that not only was the floating oil film largely removed, but more than half of the dissolved hydrocarbon was taken from the water by the peat as well, which suggests very high removal efficiency of peat compared

Table 4-7 Removal efficiency of the initially dissolved oil tests for 32 combinations

No.	Peat Type	Reaction Time (h)	Stirrer speed (rpm)	Water Temp. (°C)	Oil Volume (mL)	Particle Size	Remaining TPHs[1] (mg/L)	Dissolved oil conc. (mg/L)	Removal Efficiency (%)
1	H	0.25	200	4	8	Fine	0.9	21.5	95.8
2	H	0.25	200	22	2	Fine	2.12	7.8	72.8
3	H	12	200	4	2	Fine	2.55	12.7	79.9
4	H	12	200	22	8	Fine	4.45	63	92.9
5	H	0.25	400	4	2	Fine	1.65	14.1	88.3
6	H	0.25	400	22	8	Fine	2.15	11.1	80.6
7	H	12	400	4	8	Fine	3.35	16	79.1
8	H	12	400	22	2	Fine	5	15	66.7
9	H	0.25	200	4	2	Coarse	3.55	12.7	72.1
10	H	0.25	200	22	8	Coarse	4.8	63	92.4
11	H	12	200	4	8	Coarse	2.3	21.5	89.3
12	H	12	200	22	2	Coarse	4.45	7.8	43.1
13	H	0.25	400	4	8	Coarse	3.36	16	79.1
14	H	0.25	400	22	2	Coarse	3.34	15	77.7
15	H	12	400	4	2	Coarse	4.14	14.1	70.6
16	H	12	400	22	8	Coarse	4.12	11.1	62.9
17	HD	0.25	200	4	8	Fine	1.63	21.5	92.4
18	HD	0.25	200	22	2	Fine	1.68	7.8	78.5
19	HD	12	200	4	2	Fine	3.3	12.7	74.1
20	HD	12	200	22	8	Fine	3.92	63	93.8
21	HD	0.25	400	4	2	Fine	2.85	14.1	79.8
22	HD	0.25	400	22	8	Fine	4	11.1	64.0
23	HD	12	400	4	8	Fine	5.3	16	66.9
24	HD	12	400	22	2	Fine	5.65	15	62.3
25	HD	0.25	200	4	2	Coarse	4.82	12.7	62.1
26	HD	0.25	200	22	8	Coarse	1.23	63	98.1
27	HD	12	200	4	8	Coarse	2.16	21.5	90.1
28	HD	12	200	22	2	Coarse	2.23	7.8	71.4
29	HD	0.25	400	4	8	Coarse	3.53	16	77.9
30	HD	0.25	400	22	2	Coarse	3.92	15	73.9
31	HD	12	400	4	2	Coarse	2.95	14.1	79.1
32	HD	12	400	22	8	Coarse	4.05	11.1	63.5
Average							3.3	20.15	77.21

[1]: TPHs values are the average of original and duplicate, data retrieved from **Table C-1** in Appendix C.
Note: HD represents highly decomposed peat, H represents horticultural peat.

to 70% or 80% removal efficiency for all hydrocarbon fraction in the water in the work of Viraraghaven et al. (1988 and 1990).

Thereafter, the results were classified by eight groups from **Table 3-3** and explained as **Figure 4-10**. Group 1 to 8 represents eight combinations from **Table 3-3.** According to the **Figure 4-10**, combinations 5 and 7 obtained higher removal efficiency; the common feature of these two combinations was lower stirrer speed. When peat was applied on the surface of oil-contaminated water, equilibrium between oil droplets and peat particles was established at this stage. Lower water turbulence might have aided the adherence of oil released by peat particles when the equilibrium had been attained thereby avoiding emulsification.

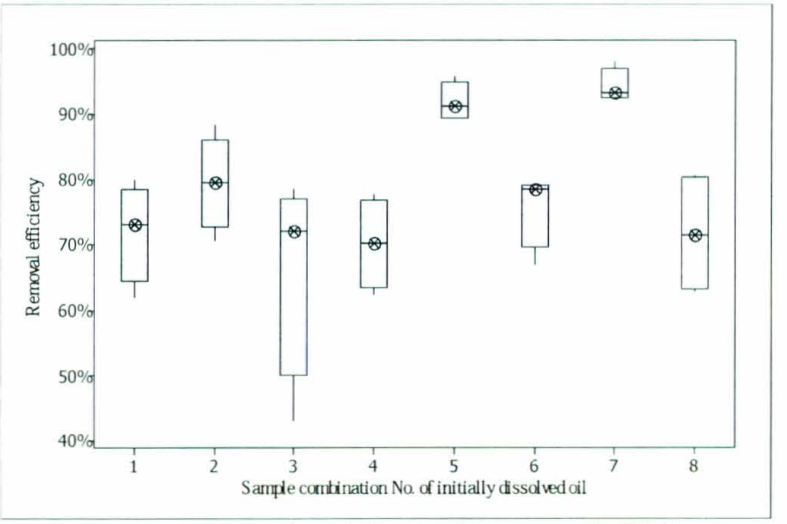


Figure 4-10 Box plot of dissolved oil removal efficiency

For a water environment with high turbulence such as combinations 4, 6 and 8, a slight difference of removal efficiency was observed. This could be due to the fact that after attainment of equilibrium between the dissolved oil and the peat particles, the

absorbing ability of the peat decreased, oil was released, and the remaining TPHs concentration increased.

The removal efficiency was only for the dissolved oil removal process, based on the assumption of complete floating oil removal. The average removal efficiency for dissolved oil was as high as 77.21% indicating the high dissolved oil adsorbing ability of peat.

Regression analyses based on peat types and particle sizes were interpreted and shown as **Figure 4-11** and **Table 4-8**.

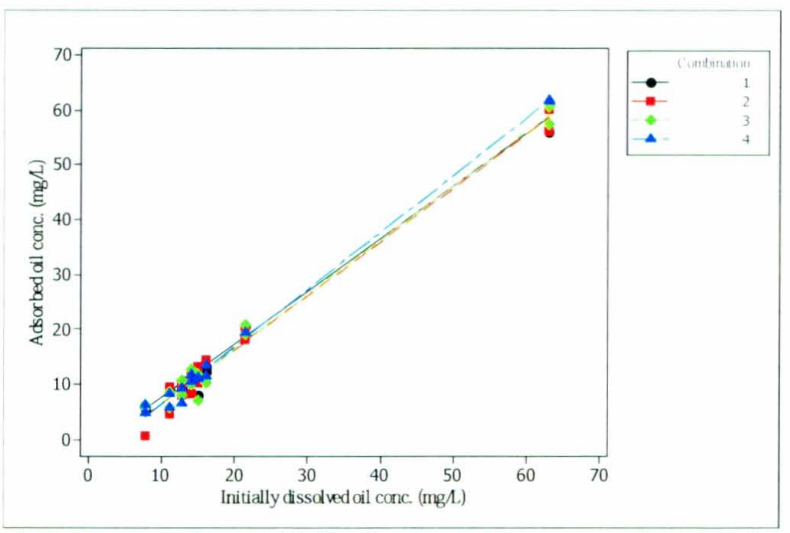


Figure 4-11 Scatter plot of initially dissolved oil conc. vs. adsorbed oil conc. by combinations

Figure 4-11 shows the regression analysis for the two peat types with different particle sizes. According to **Table 4-8**, it was observed that the slope of each regression equation was close to 1, which suggests that the difference between response (adsorbed oil conc.) and variable (initially dissolved oil conc.) was approximately equal to the absolute value of each intercept. This could be clearly seen when the regression equation

attained the value of Ads. + 2.06 = 0.965 Ini. (see Combination 1 in **Table 4-8** for example). The sum of the adsorbed oil concentration and the remaining TPHs is equal to the initially dissolved oil concentration (treat 0.965 as 1). Therefore, the absolute value of the intercept for each combination could be considered as the remaining TPHs concentration in the treated water, and experimental errors could be negligible when considering this as a rough estimation for the remaining TPHs.

Table 4-8 Initially dissolved oil removal efficiency by combinations

Combination	Peat Type	Particle size	Regression equation	Average removal efficiency
1	Horticultural	Fine	Ads.= 0.965 Ini - 2.06.	82.03%
2	Horticultural	Coarse	Ads.= 0.985 Ini - 3.45.	73.37%
3	highly Decomposed	Fine	Ads.= 0.991 Ini - 3.35.	76.46%
4	highly Decomposed	Coarse	Ads.= 1.04 Ini - 4.00.	76.99%

Notes: Ads. represents adsorbed oil concentration, Ini. represents initially dissolved oil concentration.

Numerically the best combination for initially dissolved oil removal application would be the use of fine horticultural peat in which the removal efficiency was as high as 82%. This would be the suggestion if peat type is the sole parameter. However, the four regression lines so close to each other indicates that there is only a slight difference in the remaining TPHs among the combinations.

Overall regression analysis was explained and shown as **Figure 4-12** and **Eq. 4-2**.

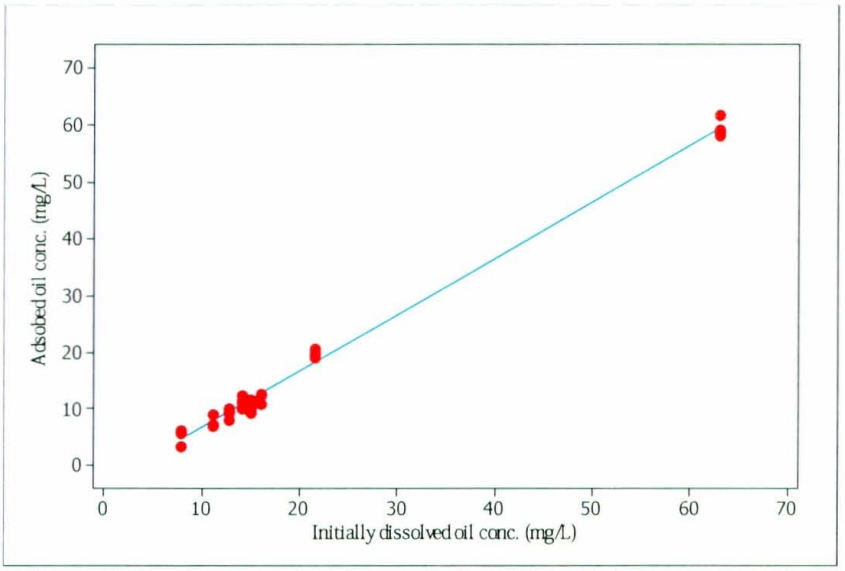


Figure 4-12 Scatter plot of adsorbed vs. dissolved oil concentration

Figure 4-12 shows the overall regression analysis for initially dissolved oil concentration and adsorbed TPHs. The coefficient of 0.996 from **Eq. 4-2** indicates that adsorbed TPHs concentration were very close to Initial TPHs concentration, which shows the high removal efficiency of peat for all combinations.

$$\text{Ads.} = -3.22 + 0.996\ \text{Ini.}$$

Eq. 4-2 Regression equation for initially dissolved oil conc. vs. adsorbed TPHs

The absolute value of the intercept suggests the approximate average difference between initially dissolved oil concentration and removed oil concentration for all situations simulated by the present experiment, which could be considered as the overall average remaining TPHs after applying peat on the surface of diesel-contaminated water.

4.6 Discussion

4.6.1 Oil Volume

Two levels (2 mL and 8 mL) of oil volume were selected to test the adsorbing ability of peat on small- and large-scale oil spill accidents. According to the effects lists as shown in **Table 4-4** for highly decomposed peat and **Table 4-6** for horticultural peat, the contribution of volume to the final response (the remaining TPHs) was respectively 0.012% and 1.08%. This indicated that oil volume is not a factor that could significantly affect the remaining TPHs.

A constant mass of 2.5 g of peat was used for all combinations. The average diesel density was 0.84 g/mL at 25°C therefore both types of peat could clean up at least 2.6 times equivalent diesel weight according to the results. The results obtained are supported by the work of Suni et al. (2006). However, the current experiment did not test the existence, if any, of a linear relationship between peat weight and oil volume.

4.6.2 Stirrer Speed

The stirrer speed was designed to simulate the effect of water turbulence. Factorial analysis indicated that strong water turbulence would increase the remaining TPHs in treated water when highly decomposed peat was used (**Figure 4-2**). This might be due to more fine particles being contained in the highly decomposed peat, which could result in faster and more effective exchange between oil droplets and peat particles; therefore oil droplets might be released more easily. However, the stirrer speed did not significantly contribute to the increase of the remaining TPHs when horticultural peat was used. Booms might be deployed to lower the water turbulence in contaminated areas and

better removal efficiency might be obtained when both types of peat are used in real situations.

4.6.3 Water Temperature

Water temperature was an important factor in the experiment since oil leakage accidents could happen anywhere with inherent local conditions. According to the experiment, removal application by horticultural peat was preferable for cold water (**Figure 4-6**). The remaining TPHs concentration increased in treated water samples at a higher temperature, which may indicate that water temperature acts as a catalyst for reactions between oil and peat. A higher temperature may accelerate the reaction between oil droplets and peat particles, and once equilibrium is reached, the absorbing ability is lost allowing oil droplets to be released and re-absorbed in a continuous cycle without any effect on removal efficiency. The equilibrium effect made it difficult to obtain or determine the optimum time at which peat should be removed from the contaminated water body. In addition, cold water is denser and so oil might float better, and the higher viscosity of cold water might cause the oil not to mix as easily. Higher water temperature causing more oil dissolved in the water might raise the difficulty of removing oil since dissolved oil is harder to be adsorbed by peat.

4.6.4 Reaction Time

According to **Figure 4-2** (a), **Figure 4-3**, **Figure 4-6** (a) and **Figure 4-7**, all results indicated that a short reaction time was the optimum time for removing diesel. In practical situations, short-time application saves time allowing for other rescue actions

such as providing extra time for filtering contaminated peat before it sinks, rescuing oil-filmed animals; avoids worse weather and current conditions and lowers the risk for clean-up crews. However, reaction time might vary when other factors such as peat type and particle size are considered.

4.6.5 Peat Particle and Peat Types

Varied diesel adsorbing ability of peat is partly due to the different size particles of the peat or the specific surface area (SSA) (Cohen et al., 1991). Normally the SSA of highly decomposed peat is larger than the SSA of horticultural peat, and the SSA of fine peat particles is larger than that of coarse peat particles regardless of the peat type (Asadi, 2009). The current experiment proved this theory with the average remaining TPHs from all combinations being the greatest (3.76 mg/L) when using coarse horticultural peat. In a real situation, clumps would need to be sufficiently ground in order to increase the SSA of the peat particles which would lead to a lower level of remaining TPHs in the water.

4.7 Comparison between the Current Experiment and Previous Studies

The comparison between previous studies and the present experiment is shown in **Table 4-9**. Several similar experiments were conducted in the past decades and achieved remarkable results. Smith et al. (1976) obtained 97% removal efficiency by blending peat and oil contaminated wastewater; compared with just spraying peat on the surface of the water as in the current study, a flow system was required for this method. The same column system was required for the experiment of Viraraghavan, et al. (1988). The column system could bring wastewater and the peat medium into complete contact in

order to activate maximum adsorbing ability and obtain the minimum concentration of remaining contaminants. However, this system was hard to apply to large volume oil spills and in open water. In the experiment done by Smith et al. (1976), chemical additives were applied, which was considered to be the introduction a second contamination during the clean-up application. Ghaly et al. (1999) conducted several experiments applying peat to the surface of the water and they obtained removal efficiency as high as 99%; however, weather and water conditions that might have had an adverse impact on removal application were not reported in their experiment. Ghaly et al. (2001) did a bioremediation experiment for oil-contaminated peat. As part of the experiment, peat was sprayed on the surface of oil-contaminated water with a thickness of 1.3 cm and removal efficiency of 99.998% was reported. However, no other factors were considered in the oil removal experiment. This oil-contaminated peat was then treated with three microbial populations and oil content reduction of 56% was obtained. This study was unique because it considered weather (temperature) and water condition (turbulence) and three other factors (oil volume, peat type and peat particle size) together. In addition, it analyzed these factors in a 2-factor factorial design.

While obtaining high diesel removal efficiency (99.99%), the current experiment analyzed weather and water conditions that could have an adverse impact on the diesel removal processes and suggested optimum external conditions to minimize the impact. In contrast to previous similar experiments, the current experiment focused on potential adverse effects on the final response and the solution for this issue rather than on contaminant removal efficiency. This method may contribute to enhance the contaminants removal efficiency and widen the thoughts for environmental protection.

This method is not only for diesel but also could be applied on other clean-up methods that might be adversely impacted by weather conditions.

In addition, not introducing chemical additives and cost-effectiveness were merits in this study. In the experiment conducted by Smith et al. (1976) it was reported that peat was pre-treated by sulfuric acid, which could cause secondary contamination when the removal process was applied. The low cost of the current experiment increases its feasibility in real situations; there was no cost except for the TPHs analysis. However, there were deficiencies due to the limitations of time and cost, which will be described in the Future Work section.

Table 4-9 Comparison between previous studies and present study

	Author	Method	Materials used	Contaminants	Application period	Removal Efficiency (concentration)
Previous Studies	Ghaly et al., 2001	Peat is applied on the surface of oil contaminated water with an oil thickness of 1.3 cm.	Kiln dried peat	Motor oil	Unknown	99.998% (remaining TPH from 1.4×10^5 mg/L to 3.1 mg/L) for an oil slick of 1.3cm in the water
	Smith et al., 1976	Peat is blended in a wastewater flow system at 25 ml/min.	Fine dried Irish peat and sulfuric acid-treated Michigan peat	~250 ppm oil-in-water emulsion, made by Exxon 260 diesel	Unknown	86% - 97% (9.0 ppm -42 ppm)
	Ghaly et al., 1999	Tap water went through oil contaminated soil and peat is placed on the top of oil-polluted water after.	Cansorb Organic Oil Absorbent type peat	Oil-contaminated water from oil-contaminated soil. Initially contaminated by No. 1 Grade A Diesel.	Unknown	29% - 76%
	Viraraghavan, et al., 1988	24-hour dried horticultural peat and dispersant are placed in a half-meter column.	Mixed Horticultural peat	Synthetic oil emulsion	8 h at 12 mL/min	91.3% - 99.6% based on different synthetic oil emulsion
Present study		Peat placed on the surface of water in the beaker with different combinations of factors (reaction time, stirrer speed, water temperature, oil volume and peat particle size).	Highly decomposed peat and horticultural peat	Irving Diesel (8.25 mg/L at 25 °C)	12 and 0.25 h	~99.99% (remained concentrations are 1.23 mg/L - 7.20 mg/L based on different combinations); average removal efficiency for initially dissolved oil was 77.2%. Optimum external conditions for higher diesel removal efficiency were obtained by experiment results and analyses.

4.7 Practical Significance of Current Experiment

Ideal results could always be obtained when conducting experiments in the laboratory because they were in a relatively low-noise environment in which risks and adverse impacts were reduced. However, the results would possibly not be as good when experiments were done in real situations. The translation from advanced technology to productivity in practice has been an issue for human beings for decades. The reasons why the experimental effectiveness might be reduced in this particular case could be weather conditions such as temperature and wind, water conditions such as waves and turbulence, or integrated factors such as the interaction between weather and water conditions. Although the results might be impacted by weather conditions, external conditions and related analyses were conducted and suggestions based on model results were given. 6 factors were involved with 2 levels for each factor; the current experiment simulated a complex environment as real as possible and analyzed the possible effects from each factor, also the solutions were provided.

Based on these considerations, five factors were taken into account in the current experiment when analyzing the final contaminant removal efficiency. Lower water temperature, lower water turbulence and shorter reaction time produced better results with the remaining TPHs being lower than when there was higher temperature and water turbulence. In practice, the method would be suitable for lake oil spills because water turbulence is lower than in an estuary or river; fast application would obtain better diesel removal efficiency. Fine horticultural peat performed better than other combinations; however, mixed particle sizes of highly decomposed peat obtained on average 2.58mg/L of TPHs (see **Figure 4-3**) and the process was labor-saving and cost -effective.

The dilemma is: that a higher number of limited external factors could improve the results, but the cost would be much greater with increased numbers. Therefore, the current experiment might not be appropriate for multiple regions or cases.

5 Conclusions and Recommendations

5.1 Summary

According to the experimental results, oil volume did not affect removal efficiency in the present experiment; this indicates that either type of peat could remove at least 2.6 times its own weight under different external conditions. Peat type and peat particle size did not contribute significantly if they were treated as individual factors. However, when particle size and reaction time were considered as a two-factor interaction, applying fine peat within a short time reached the minimum remaining TPHs concentration. Reaction time, stirrer speed and water temperature were in direct proportion with the remaining TPHs concentration if they were treated individual factors, with the remaining TPHs increasing with longer reaction time, stronger water turbulence and higher water temperature. This conclusion could be connected to the internal and external impacts. Internal impacts might be due to the chemical reaction between the functional groups of peat particles and oil-in-water/water-in-oil droplets. External impacts might be due to the catalytic function of stronger water turbulence (causing a faster reaction) and higher water temperature (making the molecular motion more active). Equilibrium could be attained during the reaction between diesel and peat.

The equilibrium could be attained in a long or short time based on the different combinations of reaction time, water turbulence and water temperature; in addition, the adsorbing/desorbing ability could vary resulting in the different remaining TPHs

concentration. Once the equilibrium was attained, an adverse reaction could take place and oil could be released by the peat particle.

5.2 Future Work

According to the present experiment, peat has been shown to be an efficient and promising sorbent for oil removal applications because of its ease of accessibility (locally available) and application with minimal pre-treatment.

The chemical composition of these two types of peat (horticultural peat and highly decomposed peat) should be investigated in the future. A detailed study could focus on the investigation of functional groups on the surface of peat particles for each type of peat because functional groups are the foundation of the chemical reaction between peat and oil; a more reasonable and scientific explanation could be obtained based on this study. Filter paper was necessary for the self-designed filtration system; however, oil that already adhered to peat particles or oil remaining in the treated water could be somehow adsorbed by the filter paper and helped to lower the remaining TPH in the treated water. Additional treatment might be required in real situations to assure the adsorbing ability and removal efficiency of peat. Further work in terms of the volume of the oil spill and meteorological conditions should be carried out. The calibration of the current experiment could be conducted in an amplified scale in real situation. Mixed peat or the combination of peat and other natural products may result in better removal efficiency. The removal process for emulsion was not tested in the current experiment. The work should also be extended to a pilot scale level for confirmation of the identified

and discussed results in this work. With that, a concrete step in the use of peat as an oil adsorbent can be taken to protect the environment in the case of an oil spill accident.

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APPENDIX A – Information required for oil spill clean-up

Table A-1 Oil Spill Accident Information Form (adopted from FSIC, 2003)

Part I	**Remark**	**Part II**	**Remark**	**Part II**	**Remark**	
1. Contact Information		**1. Boom in fast water**		Ignition time		
Name		Current Speed		Burn time		
Agency/Company		Length Deployed		Percentage oil burned		
Contact Phone/Number		Type		Percentage oiled vegetation burned		
Email		Skirt Length		Other vegetation burned		
Firefighter/HazMat Team		Angle		Air monitoring before burn		
State Agency		U in boom		LEL before burn		
Cleanup Contactor		Deflection		Distance from product		
Owner/Operator		Containment		**Air Monitoring Results**		
Federal/Agency		Protection		Product detected	Time	Distance
Other		Percent containment				
2. Weather		Percent collected				
Temperature		Quantity collected				
Wind Direction		Percentage entrainment				
Wind Speed		Secondary boom number of strings		**Air Monitoring After Burn**		
Precipitation		Type		Product Detected	Time	Distance
3.Product		Length				
Quantity		LEL before booming				
Gallons		Length of shoreline oiled				
Barrels		**2. Oil**				
Sheen Only		Oil in sewers				
Gasoline		Oil on the roadside				
Diesel Fuel		Oil in ditch				
Crude Oil		Other				

Cont'd **Table A-1**

Number 6/Heavy Oils		Water treatment plant affected?				
Cutting oils/Lube Oils		Product visible at outfall?				
Vegetable/Animal Fats		Contained at outfall?				
Others		Chemical/Foam Name				
Size/Surface Area		Time Applied				
Estimate Thickness Product		Quantity applied				
Color		Dilution				
4. Location		LEL before application				
Urban		LEL after application				
Field		LEL 1 hour after application				
Wooded		3. Burn				
Other		Terrain				
5. Event Description		Ditch				
Event Name and Date		Wetland				
Boom in water with current greater than 1 mph		Stream				
Oil/Gasoline in sewer system		Lake				
Oil/Gasoline in Ditch		Backwater				
Gasoline/Diesel on roadway		Other				
In Situ Burn		Depth of product in soil				
Other		Was the oil contained by boom?				
		What starter was used?				
		What accelerant was used?				
		What, if any, other agents were used?				

APPENDIX B – Experimental preparation

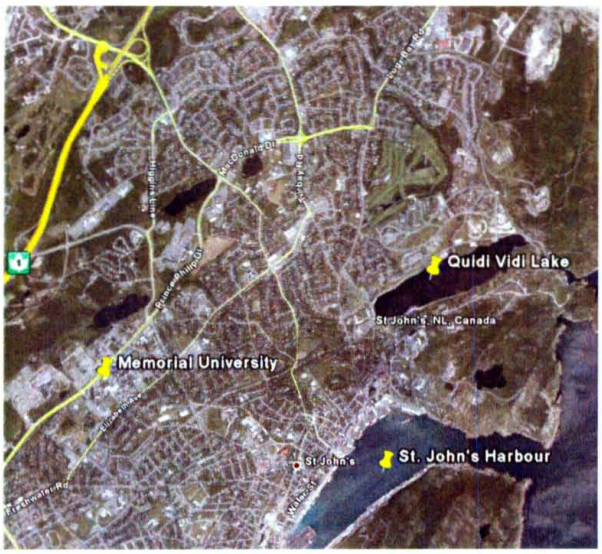

Figure B-1 Satellite view of Quidi Vidi Lake, St. John's, Newfoundland (Google Map, 2009)

APPENDIX C – TPHs data

Table C-1 Original and duplicate data of the remaining TPHs from the batch tests

Sample No.	TPHs[1] C10-C21 (mg/L)	TPHs[2] C10-C21 (mg/L)	TPHs[1] C21-C32 (mg/L)	TPHs[2] C21-C32 (mg/L)	TPHs[1] (mg/L)	TPHs[2] (mg/L)	Emulsification
1	0.34	0.36	0.5	0.6	0.84	0.96	No
2	0.98	0.95	1	1.3	1.98	2.25	No
3	1.1	1.4	0.8	1.8	1.9	3.2	No
4	1.3	5	0.6	2	1.9	7	No
5	0.81	0.58	1.1	0.8	1.91	1.38	No
6	1	1.1	0.9	1.3	1.9	2.4	No
7	1.5	1.1	2.4	1.7	3.9	2.8	Yes
8	1.5	1.9	1.6	5	3.1	6.9	Yes
9	1.3	2.3	1.2	2.3	2.5	4.6	No
10	1.9	4.4	1	2.3	2.9	6.7	No
11	0.58	0.91	0.6	2.5	1.18	3.41	No
12	1.1	1.3	0.6	5.9	1.7	7.2	No
13	0.92	1.7	0.7	3.4	1.62	5.1	No
14	0.97	1.5	0.8	3.4	1.77	4.9	No
15	1.2	0.98	1.3	4.8	2.5	5.78	Yes
16	0.74	1.8	0.9	4.8	1.64	6.6	Yes
17	0.32	0.74	0.5	1.7	0.82	2.44	No
18	0.45	1.1	1	0.8	1.45	1.9	No
19	1.6	1.1	3	0.9	4.6	2	No
20	1.6	0.94	4	1.3	5.6	2.24	No
21	1.4	1.1	2.8	0.4	4.2	1.5	No
22	1.4	2.5	1.3	2.8	2.7	5.3	No
23	3.1	2.7	2.7	2.1	5.8	4.8	Yes
24	4.3	1.4	3.8	1.8	8.1	3.2	No
25	0.64	2.1	2.8	4.1	3.44	6.2	No
26	0.57	0.72	0.6	0.56	1.17	1.28	No
27	0.72	1.2	1.4	1	2.12	2.2	No
28	0.45	1.3	1	1.7	1.45	3	No
29	1.6	0.96	2.9	1.6	4.5	2.56	No
30	0.94	1.3	3	2.6	3.94	3.9	No
31	0	1.4	2.3	2.2	2.3	3.6	Yes
32	1.1	1.4	4.1	1.5	5.2	2.9	Yes

Notes: TPHs [1] and TPHs [2] stand for original and replication data respectively.

APPENDIX D – ANOVA Table and Basic Definition of ANOVA

Table D-1 Definitions for ANOVA table

Source	Definition	Sum of square	df	Mean square	F value	P-value	Conclusion
Model		Total of the sum of squares for the terms in the model	Degrees of freedom for the model	Estimate of the model variance	Test for comparing model variance with residual (error) variance	Probability of seeing the observed F value if the null hypothesis is true. Small probability values call for rejection of the null hypothesis.	If the p-value is very small (less than given α value) then the model is significant.
Terms	Factors	The number of factorial experiments divided by 4 times the squared factor effect	Degrees of freedom for the term	Estimate of the term variance	Test for comparing term variance with residual (error) variance	The same as above	If the p-value is very small (less than given α value) then the term is significant.
Lack of fit	This is the variation of the data around the fitted model. If the model does not fit the data well, the test will show significant	Residual sum of squares after removing the pure error sum of squares	The amount of information available after accounting for blocking, model terms, and pure error	Estimate of lack of fit	Test for comparing lack of fit variance with pure error variance	The same as above	If the p-value is very small (less than given α value) then lack of fit is significant.
Pure Error	Amount of variation in the response in replicated design points	Pure error sum of squares from replicated points	The amount of information available from replicated points	Estimate of pure error variance			
Cor total	Totals of all information corrected for the mean	Sum of the squared deviations of each point from the mean	Total degrees of freedom for the experiment, minus one for the mean				

To obtain a better understanding to ANOVA and ANOVA table in the current study (**Table D-4** and **Table D-5**), **Table D-1** provides the definition of each block in the ANOVA table. Analysis of variance (ANOVA) was developed by the English statistician, R.A. Fisher (1890-1962). The initial and basic purpose of ANOVA is to test the significant difference between means. However, the world is complicated and multivariate in nature. When comparing more than two groups of populations, two-way ANOVA has been proven to be a good statistical tool.

The calculation and ANOVA table for a two-way ANOVA are shown by following example (Stat-Ease, 2007):

Factor A has levels numbered $i = 1, \ldots a$

Factor B has levels numbered $j = 1, \ldots b$

Each combination has $k = 1, \ldots n$ replications

The data can be laid out as shown in **Table D-2.**

Table D-2 The layout of the data

	$j = 1$	$j = 2$		$j = b$	Means of factor A
$i = 1$	y_{111} y_{112} $\cdots$ y_{11n} $\bar{y}_{11k}$	y_{121} y_{122} $\cdots$ y_{12n} $\bar{y}_{12k}$	$\cdots$	y_{1b1} y_{1b2} $\cdots$ y_{1bn} $\bar{y}_{1bk}$	$\bar{y}_{1\cdot\cdot}$
$i = 2$	y_{211} y_{212} $\cdots$ y_{21n} $\bar{y}_{21k}$	y_{221} y_{222} $\cdots$ y_{22n} $\bar{y}_{22k}$		y_{2b1} y_{2b2} $\cdots$ y_{2bn} $\bar{y}_{2bk}$	$\bar{y}_{2\cdot\cdot}$
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$
$i = a$	y_{a11} y_{a12} $\cdots$ y_{a1n} $\bar{y}_{a1k}$	y_{a21} y_{a22} $\cdots$ y_{a2n} $\bar{y}_{a2k}$		y_{ab1} y_{ab2} $\cdots$ y_{abn} $\bar{y}_{abk}$	$\bar{y}_{a\cdot\cdot}$
Means of factor C	$\bar{y}_{\cdot 1\cdot}$	$\bar{y}_{\cdot 2\cdot}$	$\cdots$	$\bar{y}_{\cdot b\cdot}$	$\bar{y}_{\cdots}$

The model equation for this two way ANOVA could be written as:

$y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \varepsilon_{ijk}$ for $i = 1 \ldots a$, $j = 1 \ldots b$, and $k = 1, \ldots n$

where, y_{ijk} is overall mean; α_i is the main effect of ith level of factor A; β_j is the main effect of jth level of factor B; $(\alpha\beta)_{ij}$ is the interaction of combination A and B at ith level of factor A and jth level of factor B and ε_{ijk} is the error. The calculation of a basic two-way ANOVA is shown as **Table D-3**.

Table D-3 The calculation of a basic two-way ANOVA table

Source	SS	df	MS	F
Factor A	$SSA = nb\sum_{i=1}^{a}(\bar{y}_{i\cdot\cdot} - \bar{y}_{\cdot\cdot\cdot})^2$	a-1	$MSA = \frac{SSA}{a-1}$	$F = \frac{MSA}{MSW}$
Factor B	$SSB = na\sum_{j=1}^{b}(\bar{y}_{\cdot j\cdot} - \bar{y}_{\cdot\cdot\cdot})^2$	b-1	$MSB = \frac{SSB}{b-1}$	$F = \frac{MSB}{MSW}$
Interaction AB	$SSAB = n\sum_{j=1}^{b}\sum_{i=1}^{a}(\bar{y}_{ij\cdot} - \bar{y}_{\cdot j\cdot} - \bar{y}_{i\cdot\cdot} + \bar{y}_{\cdot\cdot\cdot})^2$	(a-1)(b-1)	$MSAB = \frac{SSAB}{(a-1)(b-1)}$	$F = \frac{MSAB}{MSW}$
Within samples	$SSW = \sum_{k=1}^{n}\sum_{i=1}^{a}\sum_{j=1}^{b}(y_{ijk} - \bar{y}_{ij\cdot})^2$	$ab(n-1)$	$MSW = \frac{SSW}{ab(n-1)}$	
Total	$SST = \sum_{k-1}^{Y}\sum_{i-1}^{a}\sum_{j-1}^{b}(y_{ijk} - \bar{y}_{\cdot\cdot\cdot})^2$	N-1		

SS: sum of squares; MS: mean square; MSW: within groups mean square;

The null hypotheses tested by F value are:

Factor A (factor A has no effect) H_0: = $\alpha_1 = \alpha_2 = \ldots = \alpha_a$

Factor B (factor B has no effect) H_0: = $\beta_1 = \beta_2 = \ldots = \beta_b$

Interaction AB (no interaction) H_0: = $\alpha\beta_{11} = \alpha\beta_{12} = \ldots = \alpha\beta_{ab}$

p-value is obtained from F-table (refer to calculated F-value) and compare with α-value in order to accept or reject null hypothesis.

According to **Table D-4**, the p-value of 0.0011 implied that the model was significant. Values of "p-value" less than 0.1 (α was set as 0.1, α was the probability of the occurance of small probability event) indicated the model terms were significant. In this case factor A - reaction time, factor B - stirrer speed, the interaction of A and E - the interaction between reaction time and particle size were significant model terms.

In addition, p-values greater than 0.1 indicated that the model terms were not significant. If there are many insignificant model terms, model reduction may improve the model. In the present model, there is only one insignificant term (factor E – particle size), therefore the model was good. The lack of Fit p-value of 0.8835 implied the Lack of Fit was not significant. There was an 88.35% chance that a lack of fit F-value this large could occur due to noise (external interference which was not accounted for in the error terms). The statistical model obtained was therefore efficient and reliable for continuing further analyses of the data (StatEase, 2007).

Table D-4 ANOVA Table for highly decomposed peat

Source	Sum of square	df	Mean square	F value	p-value Prob>F
Model	4.38	4	1.09	6.35	0.0011
A-Reaction time	0.91	1	0.91	5.29	0.0297
B-Stirrer speed	2.63	1	2.63	15.25	0.0006
E-Particle size	0.15	1	0.15	0.88	0.3565
AE	0.68	1	0.68	3.93	0.0582
Residual	4.48	26	0.17		
Lack of Fit	1.18	11	0.11	0.49	0.8835
Pure Error	3.3	15	0.22		
Cor Total	8.86	30			

According to **Table D-5**, the Model p-value of 0.0178 suggested that the model was significant. In this case factor A - reaction time, factor C - water temperature, and interaction AE (the interaction of reaction time and particle size) were significant model terms. Besides, the lack of fit p-value of 0.9722 implied that the lack of fit was not significant relative to the pure error. There was a 97.22% chance that a lack of fit F-value this large could occur due to noise. This lack of fit would not affect the model analysis and results and suggested that the model was efficient and reliable to continue the further analyses of the data.

Table D-5 ANOVA Table for horticultural peat

Source	Sum of square	df	Mean square	F value	p-value Prob > F
Model	3.95	4	0.99	3.6	0.0178
A-Reaction Time	0.89	1	0.89	3.26	0.0821
C-Water Tem	0.82	1	0.82	2.97	0.096
E-Particle	0.79	1	0.79	2.87	0.1017
AE	1.45	1	1.45	5.29	0.0294
Residual	7.4	27	0.27		
Lack of Fit	1.31	11	0.12	0.31	0.9722
Pure Error	6.1	16	0.38		
Cor Total	11.35	31			

APPENDIX E – Model Validation from Design Expert 7.0®

The validation of the model was done via the necessary checks which included: checking the normal plot of the residuals; the distribution of the plot of residuals vs. predicted values; residuals vs. runs; and finally the predicted vs. the actual.

Ideally, for plot (a) the normal plot of residuals (errors) will be a straight line, indicating no abnormalities. For plot (b) the size of the residuals should be independent of their predicted values. In other words the spread of the studentized residuals (the quotient resulting from division of a residual by an estimate of its standard deviation) should be approximately the same across all levels of the predicted values and a funnel shape should not appear. For plot (c) there should not appear obvious one-way upward or downward trends. For plot (d) the points should evenly and randomly fall both sides of the line (StatEase, 2007).

According to **Figure E-1** (model validation for highly decomposed peat), experimental points were normally distributed as shown in plot (a), no S-Shape, no funnel shape was seen in plot (b), and points were randomly scattered on both sides of the line in plots (c) and (d). The four plots in **Figure E-1** suggested that the statistical model was a good representation of the data collected over the experimental range chosen. The results met the model requirements and could therefore be relied upon for prediction purposes and scale-up applications.

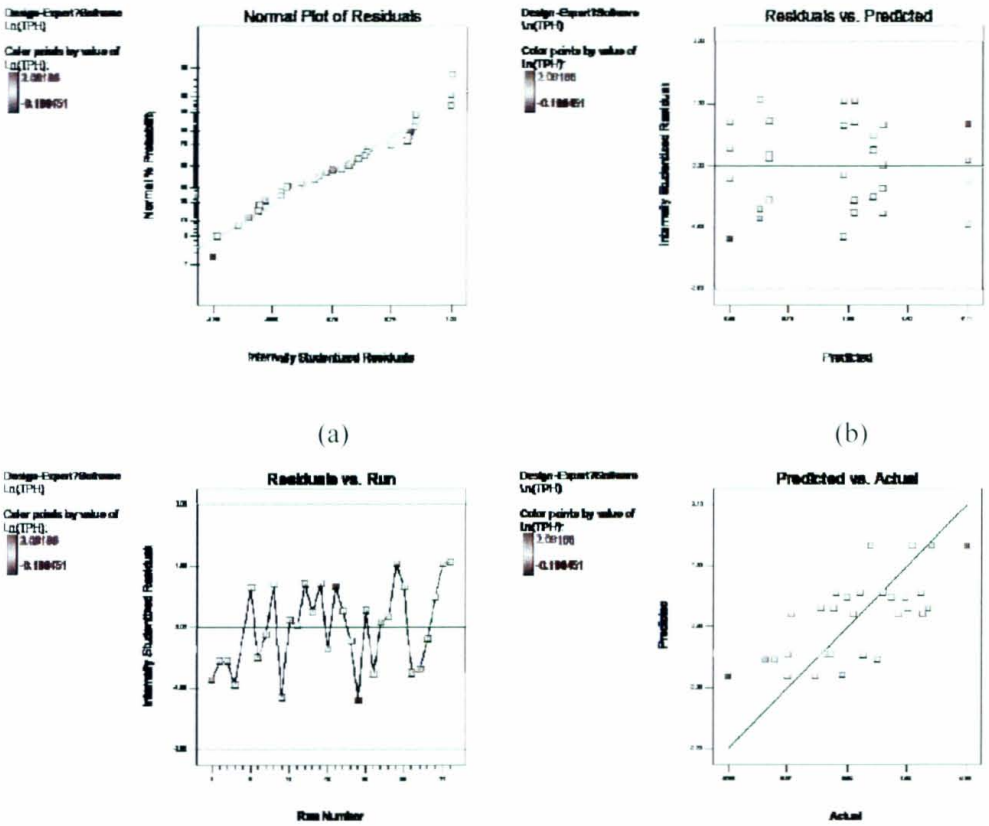

Figure E-1 (a) Normal plot of residuals; (b) Residuals vs. Predicted, (c) Residuals vs. Run; (d) Predicted vs. Actual, model validation for highly decomposed peat

Figure E-2 (model validation for horticultural peat) shows the four plots used in the diagnosis of the model validation. According to these plots, points were approximately close to the line in plot (a), no funnel shape was presented in plot (b), and points were randomly scattered on both sides of the line in plots (c) and (d). All of these indicated that the model was a good representation of the data collected over the experimental range chosen.

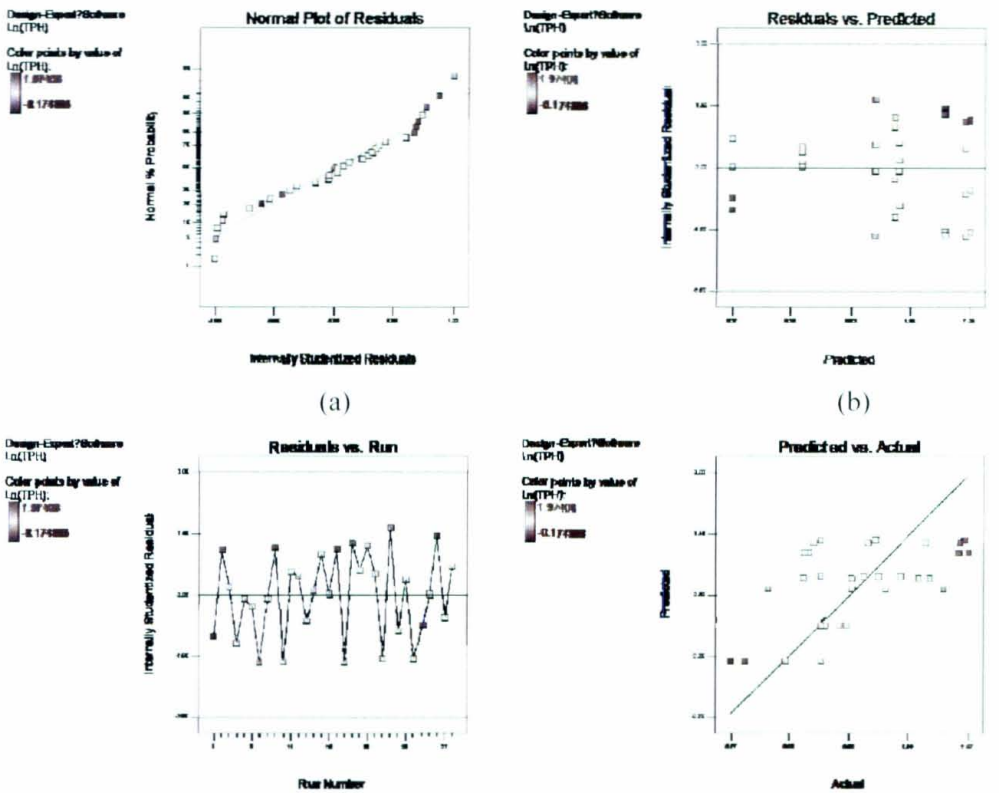

Figure E-2 (a) Normal plot of residuals; (b) residuals vs. predicted; (c) residuals vs. run; (d) predicted vs. actual, model validation for horticultural peat

APPENDIX F – Tests from Minitab 15®

1) Mann-Whitney Test

Minitab 15® has the capacity to perform the Mann-Whitney Test which is the non-parametric equivalent to the independent samples t-test. The null hypothesis for the test is H_0: the population medians (numeric values separating the higher half of a sample) are equal. The non-directional alternative hypothesis is H_1: the population medians are not equal (UWE, 2007). In the current experiment, the null hypothesis was that the results from original separation and the duplicate were the same. The α value (the probability of the occurrence of the small probability event) was set as 0.1. The point estimation (-1.75) fell between -9.7 and 2.5 at 91.7% confidential interval (indicated the reliability of an estimate was 91.7%) suggesting the null hypothesis was accepted. There was no significant difference between the original separation and the duplicate.